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SOME DOUBLE SALTS OF LEAD.

BY JOHN WHITE.

Although it has long been known that the sulphate of lead is markedly soluble in aqueous solutions of the alkaline salts of certain organic acids, such as the acetates and tartrates of ammonium and sodium, it does not appear to have been generally remarked that this property of solubility applies also to other of the difficultly soluble lead salts.

During the course of some other work dealing with compounds of lead, it was observed that lead iodide dissolves to an appreciable extent in a concentrated aqueous solution of sodium acetate, yielding, upon evaporation, a white, crystalline crust, which was found to contain both lead and iodine. Subsequent experiments have shown that the chloride and bromide of lead behave like the iodide under similar conditions.

Upon search, it was found that the literature of the subject is very meagre, this property having been previously observed by only a few investigators, and that none of the text-books of chemistry make mention of the fact. The first authentic notice of it is contained in an article by Poggiale,[1] in which he describes a complex salt as being formed by heating to-

[1] Ann. Chem. (Liebig), 56, 234 (1845); Compt. rend., 20, 1180.

gether lead chloride and basic lead acetate. To this he gives the formula $PbCl.5PbOC_2H_3O_2 + 15H_2O$. The published data concerning this salt is such as to lead to the conclusion that it was very impure. Later, Carius[1] prepared a somewhat similar compound by dissolving lead chloride in a water solution of lead acetate, to which he ascribes the formula

$$Pb\begin{cases} Cl \\ C_2H_3O_2 \end{cases} + Pb\begin{cases} C_2H_3O_2 \\ C_2H_3O_2 \end{cases} + 3H_2O.$$

Judging from the description and the analyses, there is every indication that his results and formula may be correct. About ten years later Tommasi,[2] apparently not being aware of the work of Carius, succeeded in dissolving the iodide of lead in a solution of potassium acetate, obtaining therefrom a crystalline compound to which he gave the formula

$$2Pb\begin{cases} I \\ C_2H_3O_2 \end{cases} + KC_2H_3O_2.$$

Later in this paper it will be seen that Tommasi probably had a definite compound, although his formula does not agree fully with the one there given. In the same article he calls attention to the fact that the iodide is soluble to some extent in the acetates of other bases, but he was unable to isolate any compound which may have been formed, and concluded that they acted as simple solvents. Various other investigators have observed somewhat similar behavior on the part of lead iodide, among whom Nicklés[3] and Field[4] may be especially mentioned who did not, however, get at the true condition of reaction.

The paucity of the literature upon the subject, and the uncertainty of the results obtained, suggested the advisability of undertaking a thorough investigation with the object of determining the general character of this and allied reactions and the nature and properties of the compounds, if any,

[1] Ann. Chem. (Liebig), **125**, 87 (1863).
[2] Ann. chim. phys. [4], **25**, 168 (1872); Bull. soc. chim., **17**, 337.
[3] Compt. rend., **56**, 388 (1863).
[4] J. Chem. Soc. (London), **26**, 575 (1873).

which are formed. Some of the results thus far obtained are recorded in the following pages.

The iodide was chosen as the most suitable of the halogen salts of lead to begin the experiments with, because decomposition of the resultant compound could be more readily detected by the change of color than if either the chloride or bromide were used. In the sequel this has proven to be the case, or, although the iodine compounds are less stable than the chlorine and bromine compounds, they are all white, or nearly so, whereas the decomposition-products are colored. This paper will deal only with the iodine compounds.

THEORETICAL.

Carius[1] describes the preparation of a class of compounds of the general formula $Pb\begin{matrix}X\\C_2H_3O_2\end{matrix}$, where X may be either chlorine, bromine, or iodine. To obtain these, he heated together in a sealed tube lead acetate and some alkyl halide, *e. g.*, ethyl, methyl, or methylene chloride. On heating to a proper temperature, reaction takes place, yielding an alkyl acetate and, what Carius calls, "*chloracetine of lead*," in a crystallized state. Schorlemmer[2] has prepared in a similar manner lead hexyl acetochloride, and in the course of this investigation a repetition of Carius' work has been carried out, substantiating his statements concerning the above compounds, with the exception of that containing iodine.

In attempting an explanation of the reaction, it would appear that we might apply to it the results obtained by von Ende[3] in his work upon the halogen salts of lead. He has shown that these salts dissociate into ions in two stages:

$$1.\ PbCl_2 = PbCl^{\cdot} + Cl';$$
$$2.\ PbCl^{\cdot} = Pb^{\cdot\cdot} + Cl'.$$

The first stage of ionization takes place much more readily than the second. It seems reasonable to suppose that other salts of bivalent lead dissociate likewise in two stages; if so,

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), **199**, 142 (1879).
[3] Ztschr. anorg. Chem., **26**, 129 (1901).

the formation of compounds like $Pb\begin{matrix}Cl\\C_2H_3O_2\end{matrix}$ can be readily understood, for, supposing we start with the acetate, this would dissociate thus:

1. $Pb\begin{matrix}C_2H_3O_2\\C_2H_3O_2\end{matrix} = PbC_2H_3O_2^{\cdot} + C_2H_3O_2'$;

2. $PbC_2H_3O_2^{\cdot} = Pb^{\cdot\cdot} + C_2H_3O_2'$.

If, at the point represented by reaction 1, we imagine a halogen salt to be added, reaction would naturally take place between the positive ion $PbC_2H_3O_2^{\cdot}$ and the negative ion Cl', forming $Pb\begin{matrix}Cl\\C_2H_3O_2\end{matrix}$, a comparatively undissociated alkyl acetate being formed at the same time. The reverse reaction, *viz.*, that produced by the action of an alkyl acetate, *e. g.*, ethyl acetate upon lead chloride, ought to yield a similar product; experiments have shown, however, that, because of the comparatively slight dissociation of the ethyl acetate and the very low degree of solubility of lead chloride in this, the reaction cannot be carried out in this way. To overcome the first objection, a metallic acetate was used instead of ethyl acetate, when it was found that, upon heating, a reaction does take place. It is to be presumed that the first product of this reaction is to form the compound $Pb\begin{matrix}X\\C_2H_3O_2\end{matrix}$. In reality, this compound has not been isolated in the case of the iodide, for the excess of the metallic acetate required to bring about a reaction is such as to carry it beyond this point, and there was always formed a compound of the general type,

$$\left(Pb\begin{matrix}X\\C_2H_3O_2\end{matrix} + M.C_2H_3O_2\right),$$

where X is any halogen and M any metal.

This formula has been written as a molecular compound, it being assumed that the acetoiodide of lead is formed as an inter-

mediate product. The method of formation and the decomposition of these compounds is in accord with this view, but further evidence is needed before this point can be accepted as proven.

EXPERIMENTAL.

As has been previously stated, the iodine salts are the ones to be described in this paper. These were found to be quite unstable, being easily split up by water and many other reagents. This behavior towards water probably furnishes an explanation for the fact that other investigators, notably Tommasi, were not more successful in isolating the salts formed, for, unless a large excess of the metallic acetate, and usually some acetic acid, be used in the water solution, lead iodide will either go over into a basic iodide, or, in case it goes into solution, the water is very apt to decompose the salt formed, precipitating out lead iodide again on cooling; moreover, should a double salt be obtained, in washing it in order to remove the excess of acetate, just so soon as that excess is reduced beyond a certain amount decomposition would result, again yielding lead iodide.

This fact, which was noticed early in the investigation, suggested the necessity of using some other solvent than water, but this liquid must have a very considerable solvent power for the metallic acetate used, else it would not be possible to hold in solution a large enough excess to bring any of the lead iodide into solution, without at the same time diluting to such a degree that the solvent would exert a decomposing effect. Although alcohol, either strong, or, in some cases, diluted more or less with water, was found to be admirably adapted to the purpose, it was found that for certain acetates its solvent action is too slight, and salts containing these could not be prepared. It was further observed in using various solvents, that the degree to which the metallic acetate dissolves varies, and, therefore, to this extent, the solvent itself plays an important part in determining the exact composition of the salt formed. The reaction is, in fact, a very good illustration of the law of mass action. This phase of

the problem is now under investigation and the results will appear later.

The Acetoiodide of Lead.—In accordance with the statement made above, when lead iodide and a metallic acetate, such as sodium acetate, are brought together, there results a compound $Pb\begin{matrix}I\\C_2H_3O_2\end{matrix}$ + $NaC_2H_3O_2$, it being assumed that the acetoiodide is formed as an intermediate product. If this view is correct, it ought to be possible to obtain the double salt through the interaction of the acetoiodide and the acetate. Attempts were, therefore, made to prepare the acetoiodide in order to test this. Carius[1] states that he obtained the acetoiodide by heating together in a sealed tube to 140° C. a mixture of 1 molecule ethyl iodide, slightly more than 1 molecule lead acetate, and 1 molecule acetic acid. All attempts so far made, following Carius' directions, to prepare the acetoiodide have failed. Frequently a small amount of a white, crystalline product could be observed in the tube, but invariably, while the reaction was still incomplete, decomposition set in, yielding large quantities of lead iodide in crystallized form. This precluded any possibility of securing the white substance in a condition fit either for use or analysis.[2] It was, therefore, not possible to carry out the experiment indicated above.

The Sodium Salt.—The first attempts to prepare the sodium salt were made by heating together in sealed tubes sodium acetate and lead iodide, using various liquids, *e. g.*, ethyl acetate, glacial acetic acid, alcohol, water, etc., as solvents. There was evidence of reaction in each case, and when a sufficient excess of sodium acetate was used, the lead iodide was entirely dissolved. Generally, a thin liquid, nearly colorless, was obtained, but when this was poured out of the tube it first solidified to a white, crystalline mass, then decomposed to form a yellow substance, the decomposition being accompanied by a

[1] *Loc. cit.*, p. 89.

[2] Some more recent experiments, made just as this paper was being prepared for publication, indicate that, under somewhat different conditions, possibly the acetoiodide may be obtained.

marked evolution of heat. It was not possible to handle the crystals rapidly enough to secure them.

The above experiments having shown that a reaction takes place between the two substances, other methods were made use of for securing the products of the reaction. Finally, after considerable experimentation, the following method of preparation of the sodium salt was adopted: A rather concentrated solution of sodium acetate in (about 80 per cent) alcohol was prepared by the aid of heat. This was used as the solvent and to the boiling solution recently precipitated lead iodide was added in small portions at a time, until the solution became noticeably yellow. It was observed that the previous addition of a little glacial acetic acid, usually 2 to 5 cc., very materially increased both the amount of iodide which dissolves and the readiness with which it passes into solution. If the yellow solution, after filtering, be allowed to cool in the air marked decomposition ensues, but if, instead, the air be excluded this does not happen. To this end, the solution was cooled by placing the vessel containing it in a vacuum desiccator over concentrated sulphuric acid, the exhaustion being accomplished by means of a good water-pump, and set aside to crystallize. Under these conditions white, or nearly white, crystals could be obtained.

It was attempted to determine with some degree of certainty the proportions to be used in the preparation of the crystals, but no satisfactory results could be obtained. This was due in large measure to the instability of the salt, for it was found that the satisfactoriness of the preparation depended to a considerable extent upon the method of handling. Sometimes lead iodide, sometimes sodium acetate would separate out first, although apparently similar conditions had been observed. The salt itself is apparently more soluble in the mother-liquor than either of its constituents, and the excess of one or the other of these beyond a certain amount had to be removed before the double salt began to crystallize. The approximate quantities leading to the best results were: 40 to 50 grams sodium acetate in enough 80 per cent alcohol to make a moderately concentrated solution, 2 to 5 cc. glacial

acetic acid, and 10 to 12 grams lead iodide. From this solution, on cooling, no lead iodide separated, but several crops of crystallized sodium acetate were obtained which were removed as fast as formed. If, at any time, decomposition set in, the salt could always be brought into solution again by heating with the mother-liquor. After the separation of sodium acetate had practically ceased, the solution was again brought into the vacuum-desiccator and allowed to slowly evaporate, when large, almost white crystals were obtained.

It is easy to judge of the relative purity of the several crops of sodium acetate by taking a portion of the salt, pressing out rapidly between drying-paper, then moistening with water or dilute acetic acid. Instant decomposition takes place, and since lead iodide is one of the products of the decomposition, the depth of color produced by this serves as a good qualitative test.

Several preparations of the salt were made and the crystals obtained were carefully examined each time under the microscope in order to determine if the tendency was to form a uniform product. This was found to be the case, except in one instance, to be noted later.

The crystals consist of flat, orthorhombic plates, usually admixed with a small quantity of thin, pearly, white scales, from which they were separated mechanically, the large crystals being picked out. Crystals up to 3 by 1.5 to 2 mm. in diameter were obtained. The planes were well defined, but no measurements were made, the necessary apparatus not being at hand. The crystal form and the planes usually occurring are shown in the accompanying figure.

Fig. I.

To obtain the crystals in a form suitable for analysis, they were collected on a Witt filter and washed by the aid of the pump, with a wash liquid prepared by mixing together approximately equal volumes of anhydrous ethyl acetate and ordinary strong alcohol in which a small quantity of sodium

acetate had been dissolved. This precaution was found to be necessary in order to prevent (drive back) the dissociation of the double salt, which takes place as soon as most of the excess of sodium acetate has been washed out. After washing, the crystals were immediately transferred to a watch-glass, placed in the vacuum-desiccator, and dried in a vacuum over strong sulphuric acid. The yellowish tint can be removed by shaking the crystals in a stoppered flask with anhydrous ethyl acetate and letting them stand for twenty-four hours or longer, with occasional shaking. The salt becomes white and the liquid assumes a yellowish tint. This is not, however, necessary, as comparative analyses made with the pure white and the slightly yellow crystals showed that there was practically no difference in them. The color is probably due to a very slight superficial decomposition, with formation of lead iodide.

The analyses were made as follows: The iodine was determined by dissolving, by the aid of heat, in water slightly acidulated with nitric acid and precipitating the iodine as the silver salt. For the estimation of the lead and sodium, the solution in slightly acidulated water was saturated with hydrogen sulphide, precipitating out the lead as the sulphide. This, after filtering and drying, was transferred to a weighed porcelain crucible, and oxidized by fuming nitric acid, the excess of which was evaporated off. A drop or two of sulphuric acid was added, and this was then driven off by heating at a very low temperature over a free flame. The residue was ignited gently and weighed as sulphate. The filtrate was evaporated in a platinum dish on the water-bath, the slight trace of lead sulphide filtered out, and then the evaporation carried to dryness in a weighed platinum crucible, a few drops of concentrated sulphuric acid added, this fumed off, ammonium carbonate added, and the residue gently ignited, thus obtaining the sodium in the form of the sulphate. The results proved quite satisfactory. The carbon and hydrogen were determined in the usual way, by burning with lead chromate. Following are the results obtained:

0.5585 gram substance gave 0.3273 gram $PbSO_4$ and 0.0791 gram Na_2SO_4.

0.4078 gram substance gave 0.2396 gram $PbSO_4$ and 0.0590 gram Na_2SO_4.

0.3957 gram white substance gave 0.1821 gram AgI.

0.3762 gram of the same gave 0.1723 gram AgI.

0.6849 gram pale yellow substance gave 0.3143 gram AgI.

0.2494 gram substance gave 0.1032 gram CO_2 and 0.0364 gram H_2O.[1]

0.4424 gram substance lost, after heating four and a half hours, 0.0255 gram in weight.

0.2237 gram substance lost, after heating eight hours, 0.0133 gram in weight.

The analyses lead to the formula

$$Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + NaC_2H_3O_2.\tfrac{1}{2}C_2H_4O_2.$$

	Calculated for $PbNaI(C_2H_3O_2)_2.\frac{1}{2}C_2H_4O_2$.	Found. I.	Found. II.
Pb	40.98	40.03	40.13
Na	4.57	4.59	4.69
I	25.12	24.86	24.76–24.79
C	11.89	11.28	....
H	1.60	1.64	....
$C_2H_4O_2$	5.95	5.76	5.95

The acetic acid of crystallization was determined by heating weighed portions of the pulverized substance in a double-walled vacuum air-bath, the heating liquid in the intermediate space being alcohol. Thus a temperature of 78° C., and, by means of a pump, a vacuum of 650 mm. was maintained. Under these conditions the acetic acid is driven off, about three hours sufficing to bring the substance to a constant weight. In one instance, after constant weight had been reached, water was substituted for alcohol in the bath and a further heating for three hours maintained at a temperature of 98° C., but without producing further loss of weight. If heated in the air, however, decomposition takes place rapidly, entailing a greater loss of weight. During the heating in a

[1] The second combustion was lost through an accident.

vacuum, the color changes from white to a pale sulphur-yellow; in air the substance assumes a deep yellow color.

When heated in a melting-tube the substance changes to a pale yellow color at a temperature of about 90° C., between 95° and 100° it assumes an orange-red hue, and when still further heated it sinters at 120° and finally melts, with partial decomposition, to a reddish, syrupy liquid at 124° to 125° C. On cooling again it solidifies to a lemon-yellow, crystalline mass.

Up to the present no satisfactory solvent for the salt has been found. Water decomposes it instantly, yielding first lead iodide, later a basic iodide; acids all produce decomposition with formation of lead iodide. It dissolves in hot alcohol, containing a considerable amount of sodium acetate, from which it can be again recovered. Alcohol alone, whether hot or cold, exerts no marked solvent action, but gradually produces decomposition. Anhydrous ethyl acetate is without effect, while hot benzene apparently dissolves it in small amount; hot nitrobenzene dissolves it readily, but apparently there is a reaction other than that of solution between them. In dry air, as when kept in well-closed bottles, the salt is apparently perfectly stable, but if left exposed to the air under ordinary conditions it quickly turns yellow, the moisture in the air probably causing decomposition. Light is without appreciable action.

The statement was made above that, accompanying the coarse crystals in their formation, there was always another product, crystallizing in thin, pearly, white scales, and that in at least one instance the coarser crystals did not constitute the main portion of the product. In this case the thin flakes seemed to be chiefly produced. It was at first supposed that this was mainly sodium acetate, but, a qualitative test revealing the presence of too much lead iodide, it was decided to examine the substance more closely. The conditions for the formation of this product could not be determined, for although it is always a constituent of the product obtained from the action of sodium acetate upon lead iodide, it seems not to be the principal product. The one instance in which it was such

could not be duplicated, as no particular attention had been paid to the conditions under which that reaction was carried out. This salt was separated from the coarse crystals by taking advantage of the difference in specific gravity of the two. On shaking in a stoppered flask with ethyl acetate it was observed that the coarse granules settled rapidly, while this fine and specifically lighter substance remained for a long time in suspension, and by decantation the two could be separated. After a few such treatments, the heavier portion was found to contain 24.61 per cent of iodine, thus indicating that it consisted mainly of the salt first described. The lighter portion contained 18.34 per cent of iodine. The latter was subjected several times more to the treatment, when it was found that its iodine content had become constant. It was then dried and analyzed. Following are the results obtained:

0.4158 gram substance gave 0.1856 gram $PbSO_4$.
0.3477 gram substance gave 0.1559 gram $PbSO_4$.
0.4727 gram substance gave 0.1514 gram Na_2SO_4.
0.3477 gram substance gave 0.1109 gram Na_2SO_4.
0.5179 gram substance gave 0.1803 gram AgI.

After drying for seven hours at a temperature of 78° C., and with a vacuum reading of 650 mm., it was found that 0.5261 gram substance had lost 0.0236 gram in weight.

The most probable formula deduced from the analyses is

$$Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + 3NaC_2H_3O_2.\tfrac{1}{2}C_2H_4O_2.$$

	Calculated for $PbNa_3I(C_2H_3O_2)_4.\frac{1}{2}C_2H_4O_2$.	Found. I.	Found. II.
Pb	30.93	30.48	30.62
Na	10.34	10.39	10.35
I	18.96	....	18.81
$C_2H_4O_2$	4.49	4.49	....

Although the method of purification leaves room for doubt if this be really a definite substance or a mixture of the other salt with sodium acetate, the appearance of the substance and the uniformity and close agreement of the analytical results with the calculated values for the above

compound would seem to indicate that it is in all probability a new salt. If we are right in supposing this whole class of compounds to be formed by molecular union (if the word has any significance), then it is possible to imagine the existence of a whole series of such compounds. It has already been stated (p. 5) that certain recent results obtained under different conditions lead also to this conclusion.

The Potassium Salt.—As stated in the introduction, Tommasi,[1] in his work, obtained a potassium lead acetoiodide, to which he gave the formula $2Pb\begin{matrix}I\\C_2H_3O_2\end{matrix} + KC_2H_3O_2$. This substance he prepared by dissolving 1 molecule lead iodide in a hot aqueous solution of potassium acetate, containing 2 molecules. This, on cooling, deposited a pale-yellow, crystalline mass, which he redissolved by heating with twelve times its weight of absolute alcohol and allowed to cool in a desiccator over lime. In this way he obtained a large quantity of white crystal flakes. There are no analytical results given in the article, and although the formula ascribed to the substance by Tommasi differs from that which we shall use, the general appearance and properties, as well as the methods employed in the preparation of Tommasi's salt are so nearly similar to ours as to leave but little room for doubt that they are identical but that his formula is probably incorrect.

The potassium salt is much easier of preparation than the sodium compound, but harder to purify. It is easier to prepare because it is very much less soluble in the mother-liquor and much more stable towards reagents than the sodium salt. Instead of using strong alcohol as solvent a quite dilute, almost 50 per cent, alcohol may be used. Indeed lead iodide will dissolve to a greater extent in the more dilute alcoholic solution of the acetate. To prepare the salt, make a fairly concentrated solution of potassium acetate in 50 to 60 per cent alcohol—acetic acid need not be added, for its presence seems in this case to be harmful; in the boiling solution lead iodide was dissolved in small portions at a time until the solution was

[1] *Loc. cit.*

practically saturated and no more would dissolve without long-continued heating. The cooling of the solution was carried out in a partial vacuum and generally did not proceed far before precipitation began; the mass finally became almost solid. This was redissolved by adding more alcohol and heating. From this solution beautiful, pearly-white leaflets precipitated out on cooling. For washing these an alcohol-ethyl acetate mixture was used, containing 2 to 3 per cent potassium acetate. Owing to the tendency of the crystal flakes to pack on the filter, and further, to decompose while moist, it was nearly impossible to get the salt thoroughly washed. The analyses show the presence of potassium acetate as an impurity. The drying was accomplished in the same manner as with the sodium salt and the analyses were carried out in a similar manner. The following results were obtained:

0.2463 gram substance gave 0.1494 gram $PbSO_4$ and 0.0517 gram K_2SO_4.

0.2888 gram substance gave 0.1760 gram $PbSO_4$.

0.4028 gram substance gave 0.0811 gram K_2SO_4.

0.2795 gram substance gave 0.1355 gram AgI.

0.3010 gram substance gave 0.1436 gram AgI.

A second preparation gave:

0.2868[1] gram substance gave 0.1743 gram $PbSO_4$.

0.4422[1] gram substance gave 0.2686 gram $PbSO_4$.

0.3862 gram substance gave 0.0799 gram K_2SO_4.

0.2591 gram substance gave 0.1235 gram AgI.

0.4211[1] gram substance gave 0.1648 gram CO_2 and 0.0464 gram H_2O.

0.3727[1] gram substance gave 0.1463 gram CO_2 and 0.0409 gram H_2O.

The formula deduced from the above results is

$$Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + KC_2H_3O_2.$$

[1] I am indebted to Miss Mary L. Fossler, of this University, for these results.

	Calculated for $PbKI(C_2H_3O_2)_2$.	Found. Preparation A. I.	Preparation A. II.	Preparation B. I.	Preparation B. II.
Pb	42.14	41.42	41.62	41.50	41.48
K	7.97	9.43	9.50	9.29	....
I	25.84	25.81	25.78	25.75	....
C	9.77	....	....	10.67	10.71
H	1.23	....	....	1.21	1.23

Some adhering potassium acetate probably is the occasion for the high values for potassium and carbon and the slightly low value for lead, though these may be due to an inherent error in the method of analysis used.

The heating in the vacuum-oven produced no change in weight, and showed that the salt contained no acetic acid. The same was found to be the case with one sample in which acetic acid had been used in the preparation.

When heated in a melting-tube, no change was observed up to 205° C., when the substance showed signs of sintering and turned only slightly yellow. At 208° to 208°.5 C., it melted fairly sharply to a pale, straw-colored liquid, which solidified on cooling to a white, crystalline mass, which again gave the same melting-point, thus proving that no decomposition had taken place.

From the mother-liquor, after removal of the potassium salt, there was obtained, upon evaporation, a crop of white, crystal needles, which readily turned slightly yellow on standing. The appearance and properties of this product are very closely in accord with those of the double iodide of lead and potassium described by Remsen and Herty[1] and by Wells.[2] A product which had not been specially purified gave 54.30 per cent iodine, whereas $KPbI_3.2H_2O$ requires 57.46 per cent.

The Ammonium Salt.—This was prepared in the same way as the sodium salt, except that no acetic acid was necessary, the reaction working better without it. The ammonium salt is so insoluble that it was frequently precipitated from the boiling solution, and differs from both the sodium and potassium salts in that it is not soluble in the mother-liquor on

[1] This JOURNAL, 11, 296; *Ibid.*, 14, 107.

[2] Am. J. Sci., 45, February No. (1903); "Studies from the Chemical Laboratory of Sheffield Scientific School, Yale University," Vol. I., p. 250.

heating. On account of the tendency to precipitate from the hot solution, the conditions of preparation can be varied between tolerably wide limits without affecting the nature of the product. A number of preparations was made, the same white, highly-crystalline product being obtained in each case. The method of washing and purification used was the same as for the sodium and potassium compounds. The salt is very unstable, decomposing very readily in air, especially while in the moist condition. Light also produces decomposition, so that the salt had to be protected from its action.

Generally, the product obtained was in the form of a fine, crystalline powder, but in a few instances fairly large, 1 to 2 mm. crystals were obtained. These showed very perfect crystal form, the planes being well defined. The crystals were apparently orthorhombic prisms, the accompanying figure showing the more common type.

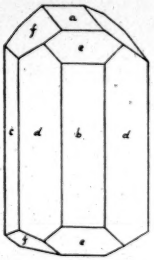


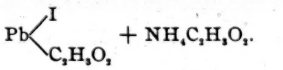
Fig. II.

In making the analyses, the methods used were the same as those previously described, except that instead of precipitating the lead as sulphide the substance was treated directly with concentrated sulphuric acid, which was fumed off and the lead thus obtained directly as sulphate. The ammonia was only tested for qualitatively, the small amount of substance at hand making a quantitative estimation somewhat uncertain. Three different preparations were analyzed, designated below as A, B, and C, respectively. The following are the results obtained :

A. 0.4639 gram substance gave 0.2327 gram AgI.
B. 0.2873 gram substance gave 0.1430 gram AgI.
0.2492 gram substance gave 0.1257 gram AgI.
0.3501 gram substance gave 0.1748 gram AgI.
0.3535 gram substance gave 0.1761 gram AgI.
0.2774 gram substance gave 0.1788 gram $PbSO_4$.
C. 0.1948 gram substance gave 0.1254 gram $PbSO_4$.

0.2583 gram substance gave 0.1669 gram $PbSO_4$.
0.2996 gram substance gave 0.1506 gram AgI.

The formula deduced from the analyses is



$$Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + NH_4C_2H_3O_2.$$

	Calculated for $PbNH_4I(C_2H_3O_2)_2$.	A.	Found. B.	C.
Pb	44.03	.....	44.02	43.96–44.12
I	27.00	27.10	26.89–27.25–26.98–26.91	27.16

Heat causes decomposition with loss of ammonia and acetic acid, leaving lead iodide. When heated in a melting-tube the salt rapidly turns to a deep lemon color, sinters at about 157° C., and melts to an amber-colored liquid at 166° to 167° C. The liquid does not again solidify unless considerably supercooled, when it forms a solid resembling lead iodide.

On evaporating the mother-liquor there was obtained a considerable quantity of long, slender, hair-like needles, forming tufts radiating from a common center. While in the solution these are pure white, but change in color so rapidly when taken out that it was impossible to obtain them in the dry state except as pale, sulphur-yellow crystals. They are extremely sensitive to light. Some of the powdered substance exposed to the action of diffused sunlight turned first yellow then brownish-red. Direct sunlight transforms this into a grayish-brown color, with liberation of iodine. The appearance and properties of the substance so strongly suggested the double ammonium lead iodide described by Wells[1] that an analysis was made, with the following results:

0.1430 gram substance gave 0.0678 gram $PbSO_4$.
0.1611 gram substance gave 0.0766 gram $PbSO_4$.
0.1402 gram substance gave 0.1512 gram AgI.
0.1374 gram substance gave 0.1476 gram AgI.

	Calculated for $NH_4PbI_3.2H_2O$.	Found. I.	II.
Pb	32.24	32.38	32.48
I	59.36	58.27	58.04

[1] Am. J. Sci., 46, July No. (1893); "Sheffield Scientific Studies, Yale University," Vol. I., p. 283.

The analysis confirms the supposition that this is a double iodide. When the needles are shaken up with alcohol containing ammonium acetate they immediately dissolve, and from the solution ammonium lead acetoiodide was obtained upon evaporation.

The formation of the above salt as a by-product of the action of ammonium acetate on lead iodide, and of a similar potassium lead compound formed under similar conditions, may be taken as evidence bearing upon the general character of the reaction, showing that at least a partial exchange between the two salts has taken place.

The Lead Salt.—In his paper dealing with the salts of the type $Pb\begin{matrix}Cl\\C_2H_3O_2\end{matrix}$, Carius[1] observes that this is decomposed by water, a white powder being first thrown out which, however, soon goes into solution; further, that the lead halides are soluble in lead acetate solution, and that in both instances the same double salt is formed. To this, based upon a chlorine estimation, he gives the formula

$$Pb\begin{matrix}Cl\\C_2H_3O_2\end{matrix} + Pb(C_2H_3O_2)_2.3H_2O,$$

and therefore a salt of the same type as those previously described in this paper. Although Carius mentions the fact that lead iodide acts like the chloride under similar conditions, he apparently did not isolate the double salt, as no description of it is given. It is doubtful if he prepared the salt at all, for a repetition of his work reveals the fact that when lead iodide is dissolved in a water solution of lead acetate practically the whole of it is converted into basic iodide. The same is indeed the case when an alcoholic solution of the acetate is used, unless a relatively large amount of acetic acid is added.

The iodide of lead is not so readily soluble in lead acetate solution as in solutions of the alkaline acetates. The following proportions, used in several instances with good success,

[1] *Loc. cit.*

will give an idea of the solubility: Fifty grams lead acetate in solution in 100 cc. 93 per cent alcohol and 30 cc. glacial acetic acid, dissolved at the boiling temperature approximately 4 grams lead iodide; an equal amount of sodium acetate will dissolve 25 grams of the iodide. The solution in lead acetate does not have to be cooled in a partial vacuum, as it exhibits but small tendency to decompose so long as it is in contact with the acetate solution. The salt obtained was well crystallized, forming well-defined, monoclinic prisms. The forms most frequently observed are shown in the accompanying figure. Occasionally, well-defined, interpenetration

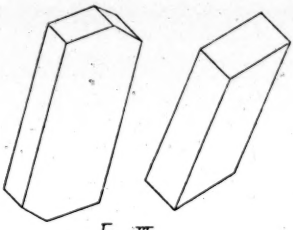


Fig. III.

twins were obtained, the individuals being arranged at right angles in the form of a Latin cross. The washing of the crystals is most readily accomplished by decantation, after shaking or stirring with absolute alcohol containing a trace of lead acetate, the final washing being carried out on a Witt filter by aid of the pump. The crystals were then dried in a vacuum over sulphuric acid. They are stable in dry air, but are decomposed by water and other reagents. The analyses were made in the same manner as with the ammonium salt and gave the following results, two samples being analyzed:

A. 0.1447 gram substance gave 0.1201 gram $PbSO_4$.
0.1279 gram substance gave 0.1055 gram $PbSO_4$.
0.2620 gram substance gave 0.0792 gram AgI.

After a further washing, the same substance gave:
0.3134 gram substance gave 0.0960 gram $PbSO_4$.
0.1523 gram substance gave 0.1263 gram AgI.

B. 0.1096 gram substance gave 0.0907 gram AgI.

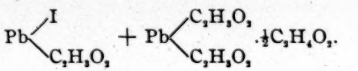
0.1074 gram substance gave 0.0333 gram $PbSO_4$.

0.7587[1] gram substance gave 0.2866 gram CO_2 and 0.1024 gram H_2O.

0.3256[1] gram substance gave 0.1259 gram CO_2 and 0.0424 gram H_2O.

On heating in a vacuum-bath at 77° C., the substance rapidly lost in weight up to a certain point, after which a very slow further loss was observed. 0.8712 gram lost 0.0327 gram. This corresponds very closely to the calculated loss required by the formula given. All compounds containing lead acetate show this gradual loss, probably caused by decomposition.

The analyses indicate the formula



	Calculated for $Pb_3I(C_2H_3O_2)_3.\frac{1}{2}C_2H_4O_2$.	Found. A.	B.
Pb	55.34	56.67–56.63–56.51	56.33
I	16.96	16.33–16.55	16.75
C	11.23	....	10.31–10.54
H	1.48	....	1.51–1.46
$C_2H_4O_2$	4.01	3.75+	....

When the salt was heated in a melting-tube it assumed a slight yellowish tint with signs of sintering at about 180° C.; at 192° it became pasty and melted slowly to a clear amber-colored, very viscous liquid at 202° to 205° C. No visible decomposition took place during the heating.

The Action of Solvents.—It has been stated that most of the substances commonly employed as solvents exert a decomposing action upon the double acetoiodides. This is especially the case with water, the alcohols, and the acids, while anhydrous ethereal salts and hydrocarbons seem to have little or no action. In consequence of this it has not been possible to determine the molecular weights of the salts and thus test the correctness of the formulas given. The decomposi-

[1] These analyses were made for me by Miss Fossler.

tion-products produced by water and alcohol were studied, however, with the idea of obtaining additional evidence bearing upon the structure. For this purpose the sodium, potassium, and ammonium salts were pulverized and shaken up in stoppered flasks with water and with absolute (96 to 98 per cent) alcohol, respectively, the time of extraction varying from 24 hours to six days.

In each instance the action of water was to produce an almost instantaneous decomposition, yielding lead iodide, shown by the orange-yellow color characteristic of this substance in the amorphous state. In a short time, however, the color began to change, turning much lighter in hue. This change proceeds very slowly, the time required for its completion varying with the size of the particles and with the individual salt, the potassium salt usually reacting more slowly than the others. At the end the color was a light sulphur-yellow. The following analyses of the residues obtained from the sodium, potassium, and ammonium salts—designated in the table as A, B, and C, respectively—show that this is a basic iodide :

	Calculated for PbI(OH).	Found. A.	B.	C.
Pb	58.98	58.58	....	58.97
I	36.16	36.44	36.13–36.21	36.16

The action of absolute alcohol upon the three double salts was, in general, of a character similar to that of water, but in this instance the nature of the individual salt seemed to play an important rôle, for it was found that the potassium salt, which is easiest of the three to prepare, showed almost no action with alcohol, there being scarcely any change in color even after several days digestion, and an iodine estimation gave 25.74 per cent iodine, the original salt containing 25.84 per cent, thus showing that no decomposition had resulted. The ammonium salt, which stands next to the potassium salt in ease of preparation, showed, after an equal time of digestion, a slight decomposition. The residue gave 30.73 per cent iodine, while the original salt contains 27 per cent. The decomposition in the case of the sodium salt was almost

complete, giving 33.64 per cent of iodine, while the original salt contained 25.12 per cent and the basic iodide 36.16 per cent.

It appears as if there were a tendency to reach a state of equilibrium, for in several instances, although the time of digestion varied, the composition of the residue was the same. This point has not yet been thoroughly tested.

A study of these decomposition reactions suggests that the first action of the solvent is to split up the double salt into its components:

1. $\left(Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + M.C_2H_3O_2 \right) =$

$$Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + M.C_2H_3O_2.$$

This reaction will proceed more or less slowly according to the degree of solubility of the double salt and of the metallic acetate formed. Subsequent to this a second reaction takes place, yielding lead iodide:

2. $$2Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} = PbI_2 + Pb(C_2H_3O_2)_2.$$

It is not quite so easy to follow the reactions involved in the formation of the basic iodide. There are two possible ways in which it could be regarded, *e. g.*:

a. $PbI_2 + H_2O = PbI(OH) + HI;$

b. $Pb\begin{matrix} I \\ C_2H_3O_2 \end{matrix} + H_2O = PbI(OH) + H.C_2H_3O_2.$

If the first of these is correct, the presence of iodide in the filtrate ought to be possible of detection. As a matter of fact, tests show only such traces of these as can be accounted for from the solubility of lead iodide. It ought further to be possible to transform freshly precipitated lead iodide into the basic salt by the action of water. Experiment shows that neither cold nor hot water has this effect to any extent.

Reaction *b* can be regarded as true only by assuming that reaction 2 above is reversible, for there can be no doubt that the first action of water is to yield lead iodide, which can only be transformed into the basic iodide by supposing that the reaction first reverses itself and then the acetoiodide formed is acted upon by water in the sense indicated in reaction *b*. Assuming this to be correct, reaction 2 should be written

$$2Pb\begin{matrix}I\\ C_2H_3O_2\end{matrix} \rightleftharpoons PbI_2 + Pb(C_2H_3O_2)_2.$$

This reaction would take place at first very readily in the sense from left to right on account of the instability of the acetoiodide and the insolubility of the lead iodide. The conversion, however, of the iodide into the less soluble basic iodide would proceed much more slowly because of the insolubility of the iodide and the small active mass of the lead acetate. It was found that the addition of lead acetate very materially hastened the conversion into the basic salt. Indeed it was found easily possible to transform freshly precipitated lead iodide into basic iodide by shaking with cold water containing a considerable excess of lead acetate. Other acetates produce a like result, but less readily, indicating that, in all probability, lead acetate must be first formed. These experiments all tend to show the reversibility of the above reactions. That reaction *b* takes place is indicated by the presence of acetic acid in the filtrate, which was easily proven. An addition of acetic acid should have the tendency to prevent this. Experiments carried out in strong alcohol indicated the correctness of the supposition, for an excess of acetic acid prevented the conversion of the iodide into basic iodide. It was found, however, that if the glacial acetic acid used be added in small quantities at a time and thoroughly mixed by shaking, a very considerable amount could be added without preventing the formation of the basic iodide. This was to be expected, for the dissociation of the acid is so slight in comparison with that of its salts that a large excess of it would be needed to counteract the influence of the lead acetate in causing reaction 2 to reverse itself.

The above discussion is based upon the primary assumption that the double salts are to be regarded as molecular compounds, containing the molecule $Pb\begin{matrix}I\\C_7H_5O_2\end{matrix}$. The observed facts are so well in accord with this, that, taken in conjunction with the methods of formation, they indicate the strong probability of the correctness of the assumption. It is hoped that, by the preparation of the acetoiodide, additional evidence may be obtained bearing upon this point, which cannot yet be regarded as fully established. The investigation is still in progress and it is hoped that this evidence may be soon forthcoming.

UNIV. OF NEBRASKA,
LINCOLN, June, 1903.

A FURTHER INVESTIGATION OF PARATOLUENEDIAZONIUM SULPHATE AND OF THE ACTION OF SULPHURIC ACID ON THE METHYL ETHER OF PARACRESOL.[1]

BY GELLERT ALLEMAN.

This investigation is in part a continuation of one by Chamberlain, the results of which have already been published.[2] Chamberlain found that by decomposing paratoluenediazonium nitrate or sulphate with methyl alcohol under ordinary atmospheric pressure, as well as under diminished or increased pressure, both paramethoxytoluene and toluene were formed. He also confirmed the observation of Remsen and Dashiell[3] that lowering the pressure favors the hydrogen reaction in the case of the nitrate.

Preparation of Paratoluenediazonium Sulphate.

One hundred grams of paratoluidine were placed in an Er-

[1] From the author's dissertation submitted, June, 1897, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

[2] This JOURNAL, 19, 531.

[3] *Ibid.*, 15, 301.

lenmeyer flask of 1 liter capacity, and 500 grams of anhydrous methyl alcohol added. As soon as complete solution took place 100 grams concentrated sulphuric acid were added by means of a dropping-funnel, allowing only a few drops into the flask at one time. Even with the slow addition of the acid and constant shaking of the flask, it was found necessary to place the flask in cold water to prevent loss of the alcohol on account of the heat generated by the reaction. As soon as a slight excess of sulphuric acid is added, the precipitate of paratoluidine sulphate which first separates goes into solution and does not again appear when the flask is placed in water containing ice.

The flask is then surrounded by ice-water and a rapid current of nitrous fumes passed through the solution for about thirty minutes. The fumes were cooled before being conducted into the vessel by first passing them through two gas bottles which were placed in cold water. After a time, crystals of paratoluenediazonium sulphate appear in the flask. They have a red color, but on being washed with ether the color disappears, showing the crystals to be glistening, snow-white flakes. The fumes are conducted through the solution till a few drops of the removed liquid, on treatment with dilute caustic soda, no longer give the odor of paratoluidine.

The diazo compound, when dry, is a comparatively stable body. Crystals were kept in a desiccator for six weeks without the least evidence of decomposition. If the crystals are filtered off and the filtrate is allowed to stand in a cool place, perfectly transparent, almost colorless prisms crystallize from the solution.

Decomposition of the Diazonium Compound with Methyl Alcohol.

Instead of taking the crystals of the diazonium sulphate out of the flask and purifying them by washing with ether and then effecting the decomposition, as is usually done in analogous cases, the flask was provided with a return-condenser and placed on a water-bath. Decomposition began at the ordinary temperature, but it was slight. At about 60° the

decomposition was rapid and the reaction had to be checked at times by pouring cold water on the outside of the flask. After the evolution of gas had almost ceased, the temperature was raised and the liquid boiled rapidly for twenty minutes in order to make sure that the decomposition was complete.

It will be seen from the above statements that the decomposition was effected in the presence of all those compounds which were formed in the flask during the diazotizing process.

Separation and Purification of the Methyl Ether of Paracresol.

After it was judged that the decomposition had been completely effected, several portions were placed in a large balloon flask provided with a Hempel tube about 3 feet high. The methyl alcohol was then distilled and some toluene came over with it, showing that the hydrogen reaction had also taken place. When the distillation was conducted too fast it was found that some of the oil came over with the alcohol. As soon as the thermometer at the top of the Hempel tube rose above 64° the distillation was discontinued and, after the solution had cooled somewhat, water was added to the flask. The distillation was then continued and quite a quantity of methyl alcohol passed over, showing that methyl sulphuric acid was, in all probability, formed, and that it broke down on the addition of water. After the methyl alcohol was removed as completely as possible by this method, the contents still remaining were treated with about twice the volume of water. The flask was then connected with a condenser, placed on a sand-bath, and heated almost to the boiling-point of the liquid contained in it. On passing steam through the mixture, a yellow oil came over with the distillate. This oil has an extremely great surface-tension. When nearly all of the oil had passed over it was noticed that the last portions were of a red color. The oil was then separated by means of a separating-funnel, dried with calcium chloride, placed in a distilling-bulb, and, after several distillations, a product was obtained which boiled at 174° to 176°. This is the methyl ether of paracresol described by Körner,[1] and also obtained

[1] Ztschr. Chem., 1868, p. 326.

by Chamberlain,[1] who gives its boiling-point as 174°.5 (corr.). Its identity was established by the formation of anisic acid when it was oxidized by potassium permanganate.

It was thought that probably the oil which came over above 180° might have its boiling-point raised by the presence of nitro-compounds and for the purpose of removing the latter, in case they were present, the whole portion of the high-boiling oil was treated with granulated tin and hydrochloric acid. After treatment in this manner it was washed repeatedly with water and finally dried with calcium chloride. It was then distilled and nearly the entire portion passed over between 174° and 176°, showing that the rise in the boiling-point of a portion of the oil was undoubtedly due to the influence of nitro-compounds which can be removed by the well-known method above described.

The tar which remained in the flask into which steam had been passed was dissolved in alcohol and the alcohol slowly evaporated, but no crystals were obtained. It was then treated with ligroin, from which yellow needles separated. These needles melted at 74° to 79°. Chamberlain investigated this tarry material, and found that it contained dinitroparacresol, ($CH_3.NO_2.OH.NO_2$ 1 : 3 : 4 : 5). He found the melting-point of this substance to be 80°.5 (corr.), and accounts for its formation by the fact that nitric acid is formed in the flask and acts on the paramethoxytoluene. He obtained the dinitroparacresol by the treatment of the methyl ether of paracresol with strong nitric acid and glacial acetic acid.

Action of Sulphuric Acid on Paramethoxytoluene.

The paramethoxytoluene was poured into pure concentrated sulphuric acid contained in an Erlenmeyer flask. The proportions in which the two compounds were brought together were 3 grams of sulphuric acid to 1 gram of paramethoxytoluene. The mixture assumed a dark-red color and became warm, indicating that some action took place at the ordinary temperature. The flask was placed on a water-bath and heated till a few drops of its contents dissolved in water

[1] *Loc. cit.*

without cloudiness, showing that the paramethoxytoluene had been completely transformed into a sulphonic acid. On cooling, part of the sulphonic acid separated as yellow crystals.

The sulphonic acid was converted into the barium salt re-repeatedly. This is a pure white, semi-crystalline material, very soluble in cold water, and insoluble in alcohol. Attempts to obtain definite crystals by crystallizing the salt under different conditions of concentration gave negative results.

Preparation of Paramethoxymetatoluenesulphonic Acid.

The acid was separated by adding to the aqueous solution of the barium salt above described sufficient dilute sulphuric acid to exactly precipitate the barium. The acid is extremely soluble in water—one part dissolving in about half its weight of water. It is almost insoluble in ether, benzene, and ligroin, but dissolves readily in methyl and ethyl alcohol and hot acetone. From water it separates at first in the form of yellow, flaked crystals. The color can be removed by washing the acid with cold anhydrous ether. If, after treatment in this way, it is crystallized from alcohol, perfectly colorless, long prisms can be obtained, which melt at 105° to 108°. The prisms have a hexagonal shape.

Sodium Salt, $C_6H_3\begin{cases}CH_3\\SO_3ONa\\OCH_3\end{cases} + \frac{1}{2}H_2O$.—This salt was made by exactly neutralizing an aqueous solution of the free sulphonic acid by means of sodium carbonate. The salt at first crystallized in small, orange-colored needles. Upon recrystallizing, colorless prisms were obtained. If allowed to stand in the air any length of time they effloresce.

Another sodium salt was prepared by exactly precipitating the barium, in an aqueous solution of the barium salt, by means of a dilute solution of sodium sulphate. After filtering off the barium sulphate and evaporating the solution to a small volume, perfectly transparent, colorless needles separa-

ted. These, on exposure to the air, also lost water and turned white.

Analyses show that both of the salts prepared as described above are identical in their composition. They are insoluble in strong, boiling alcohol. Estimations of sodium and water gave the following results:

	Calculated for $C_6H_3(CH_3)(OCH_3)-SO_3Na+\frac{1}{2}H_2O$.	Found. Salt from free acid.		Salt from Ba salt.	
		I.	II.	III.	IV.
H_2O	3.86	3.96	3.98	3.89	3.92
Na	9.87	9.88	9.72	10.04	10.07

Potassium Salt, $C_6H_3(CH_3)(OCH_3)-SO_3OK+2H_2O$.—A hot solution of the free sulphonic acid was carefully neutralized with pure potassium carbonate. Transparent, slightly red needles were first obtained, and, on recrystallizing these, large prisms, which had a slight yellow color, separated. The salt was purified by boiling it with 50 per cent alcohol, from which it crystallizes, when the solution is concentrated, in colorless needles, which radiate from the central point; from dilute solutions, in thin flakes. The salt is much less soluble in water than any of the other salts of this acid. It is insoluble in boiling strong alcohol.

0.1547 gram of salt lost, at 200°, 0.0206 gram H_2O and gave 0.0483 gram K_2SO_4 or 0.02165 gram K.

0.2582 gram salt lost, at 200°, 0.0339 gram H_2O and gave 0.0812 gram K_2SO_4 or 0.0364 gram K.

	Calculated for $C_6H_3(CH_3)(OCH_3)-SO_3K+2H_2O$.	Found. I.	II.
H_2O	13.05	13.33	13.13
K	14.13	14.00	14.09

Calcium Salt, $\left(C_6H_3(CH_3)(OCH_3)-SO_3\right)_2Ca+4\frac{1}{2}C_2H_5OH$.—This salt crystallizes from alcohol, in which it is easily soluble, in color-

less, transparent crystals, which have the appearance of very much distorted octahedrons. After some time it was noticed that acicular crystals began to separate in the same solution. At this point the crystals first formed were removed for analysis.

Great difficulty was experienced in the analysis of this salt, owing to the fact that the last molecule of alcohol seems to be held more firmly than the others, and comes off only on long-continued heating at a high temperature. The heating in several cases was stopped before all the alcohol was driven off, as a slight change in color seemed to indicate that the salt was about to undergo decomposition. The results for calcium in all these cases were low when calculated on the basis of the alcohol-free salt, but when the calculation was made on the basis of the salt with alcohol of crystallization the results for calcium in three cases were constant.

0.2299 gram salt lost, at 210°, 0.0716 gram alcohol and gave 0.0485 gram $CaSO_4$, or 0.01426 gram Ca.

0.161 gram salt lost, at 210°, 0.0515 gram alcohol and gave 0.0332 gram $CaSO_4$, or 0.00976 gram Ca.

	Calculated for $\left(C_6H_5-\overset{CH_3}{\underset{OCH_3}{SO_3}}\right)_2Ca + 4\frac{1}{2}C_2H_5.OH$.	Found. I.	II.
$C_2H_5.OH$	31.41	31.15	31.99
Ca	6.07	6.20	6.06

The needles which separated last were again dissolved, after which crystals came down like the crystals first obtained and analyzed. There is reason for the belief that the two forms of crystals obtained were due to the differing concentration of the solution and that the needle-like crystals contained a different number of molecules of alcohol from those shaped somewhat like the distorted octahedron. (The latter crystals are not octahedrons, but simply present a striking resemblance to distorted octahedrons.) A salt of this nature, concerning which experimental data will be given, will be described later.

The salt which was crystallized from alcohol was powdered and heated for five hours in a drying-oven at 200°, in order

to remove the alcohol. It was then dissolved in water, and, on slow evaporation, transparent, colorless, long, monoclinic prisms separated. These crystals can remain in the air several days without any sign of efflorescing.

The utmost difficulty was experienced in obtaining anything like satisfactory results for the water contained in the salt. At a temperature of 210° the salt had a constant weight, but the calcium in every case was about 0.5 per cent low when calculated on the basis of the anhydrous salt. Long heating at 230° to 240° was found necessary in order to obtain the salt in an anhydrous condition. Extreme care had to be exercised, as the salt undergoes decomposition at almost the same temperature at which it loses its last trace of water.

0.2364 gram salt gave 0.0479 gram $CaSO_4$ or 0.01408 gram Ca.

0.2381 gram salt lost, at 235°, 0.0795 gram H_2O and gave 0.0482 gram $CaSO_4$, or 0.01417 gram Ca.

0.1904 gram salt lost, at 240°, 0.0622 gram H_2O and gave 0.0396 gram $CaSO_4$, or 0.01164 gram Ca.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Ca + 12H_2O$.	Found. I.	II.	III.
H_2O	32.83	....	33.39	32.66
Ca	6.08	5.96	5.95	6.11

Magnesium Salt, $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Mg + 8H_2O$.—To a hot aqueous solution of the free sulphonic acid finely powdered magnesium oxide was added until the solution was exactly neutral. Light red, transparent, elongated prisms separated which, on second crystallization, were obtained in a colorless condition. The salt, on long exposure to air, lost part of its water of crystallization. The anhydrous salt, on exposure to air, again took up water, but the amount it absorbed was not determined.

0.2142 gram salt lost, at 150°, 0.0546 gram H_2O and gave 0.0146 gram MgO, or 0.00876 gram Mg.

0.202 gram salt lost, at 150°, 0.051 gram H_2O and gave 0.0137 gram MgO, or 0.0082 gram Mg.

	Calculated for $\left(C_6H_3\begin{matrix}CH_3\\SO_3\\OCH_3\end{matrix}\right)_2Mg + 8H_2O$.	Found. I.	II.
H_2O	25.26	25.24	25.49
Mg	4.21	4.09	4.07

Copper Salt, $\left(C_6H_3\begin{matrix}CH_3\\SO_3\\OCH_3\end{matrix}\right)_2Cu + 6\frac{1}{2}H_2O$.—Two copper salts were made, the one by exactly precipitating the barium, in an aqueous solution of the barium salt, by means of a dilute solution of copper sulphate, and allowing the copper salt to crystallize slowly after filtering off the barium sulphate. The salt thus obtained had a slight blue color and was composed of needles.

Another salt was made by neutralizing the aqueous solution of the free sulphonic acid with freshly prepared copper oxide. The crystals of the salt thus prepared were needles having a slight green color. Probably neither of the salts was pure, but analyses showed both to be identical in composition. The results given under I. and II. are for the salt prepared by the second method; that under III. for the salt made by neutralizing the barium salt with copper sulphate.

0.2286 gram salt lost, at 150°, 0.0461 gram H_2O and gave 0.0312 gram CuO, or 0.0249 gram Cu.

0.1803 gram salt lost, at 150°, 0.0361 gram H_2O and gave 0.025 gram CuO, or 0.0199 gram Cu.

0.1582 gram salt lost, at 150°, 0.0321 gram H_2O and gave 0.021 gram CuO, or 0.01675 gram Cu.

	Calculated for $\left(C_6H_3\begin{matrix}CH_3\\SO_3\\OCH_3\end{matrix}\right)_2Cu + 6\frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	20.09	20.16	20.02	20.21
Cu	10.85	10.88	11.16	10.59

Zinc Salt, $\left(C_6H_3\begin{cases}CH_3\\SO_3\\OCH_3\end{cases}\right)_2Zn + 6\frac{1}{2}H_2O$.—This salt was prepared by neutralizing an aqueous solution of the free acid with zinc carbonate. After recrystallizing the yellow crystals which first separated, perfectly colorless prisms were obtained. The crystals effloresce on exposure to air.

0.208 gram salt lost, at 125°, 0.0421 gram H_2O and gave 0.0282 gram ZnO, or 0.2363 gram Zn.

0.2041 gram salt lost, at 125°, 0.0411 gram H_2O and gave 0.0278 gram ZnO, or 0.0223 gram Zn.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\OCH_3\end{cases}\right)_2Zn + 6\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	20.03	20.24	20.13
Zn	11.13	11.36	10.93

Lead Salt, $\left(C_6H_3\begin{cases}CH_3\\SO_3\\OCH_3\end{cases}\right)_2Pb + 3H_2O$. — The lead salt was prepared by adding lead carbonate to a hot aqueous solution of the free acid. The crystals separating at first were composed of light-yellow, radiating fibers. These crystals were dissolved in strong alcohol in order to remove any lead carbonate or sulphate which might have crystallized with them. The alcoholic solution was then evaporated to dryness and the salt again crystallized from water, from which it was obtained in colorless needles that radiated from a central point.

0.2102 gram salt lost, at 115°, 0.0169 gram H_2O and gave 0.0964 gram $PbSO_4$, or 0.06579 gram Pb.

0.230 gram salt lost, at 115°, 0.0185 gram H_2O and gave 0.1057 gram $PbSO_4$, or 0.07214 gram Pb.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\OCH_3\end{cases}\right)_2Pb + 3H_2O$.	Found. I.	II.
H_2O	8.15	8.04	8.05
Pb	31.16	31.30	31.37

Fusion of Paramethoxymetatoluenesulphonic Acid with Potassium Hydroxide.

About 30 grams of potassium hydroxide were melted in a silver crucible and about 10 grams of the free acid, dissolved in water, were gradually added, after the temperature had fallen sufficiently to prevent spurting. The mass assumed a dark-red color, and after being heated for one-half hour at 180° to 200°, gradually turned white. A small portion of the mass was taken out, dissolved in water, and acidified with dilute hydrochloric acid. No odor of sulphur dioxide being perceptible, the fusion was continued, tests for sulphur dioxide being made at intervals of about five minutes. After heating for about an hour at the temperature above mentioned, a trace of sulphur dioxide was noticed, when a portion of the mass was dissolved in water and acidified with hydrochloric acid. The fusion was then discontinued and the entire mass dissolved in water and acidified with hydrochloric acid. Only a small amount of sulphur dioxide was given off. The solution was evaporated to dryness, the residue heated in a drying-oven at 130°, finely powdered, and extracted for ten minutes with boiling absolute alcohol. From the alcoholic filtrate, white needles separated. These needles were purified by dissolving them again in absolute alcohol, in which they are difficultly soluble. From concentrated aqueous solutions the substance separates in colorless, orthorhombic prisms. In this manner crystals 20 x 5 x 2 mm. were obtained. Analysis showed the substance to be a potassium salt. The salt crystallized from water melts at 244° and decomposes at 247°. The twin crystals form crosses and, in appearance, resemble the mineral staurolite.

0.2164 gram salt gave off, at 170°, 0.0297 gram H_2O and 0.0715 gram K_2SO_4, or 0.03204 gram K.

0.226 gram salt lost, at 190°, 0.0319 gram H_2O and gave 0.075 gram K_2SO_4, or 0.03361 gram K. The salt in this determination was slightly fused, which accounts for the high result for H_2O.

	Calculated for $C_6H_3(CH_3)(OH)-SO_2OK + 2H_2O$.	Found. I.	Found. II.
H_2O	13.74	13.77	14.11
K	14.88	14.83	14.81

Further Action of Potassium Hydroxide on Paramethoxymetatoluenesulphonic Acid.

From the experiment above described it will be seen that the methoxy group is the least stable, and is most easily replaced by hydroxyl. The sulphonic acid group is very stable in this compound, and it requires a high temperature and fusion for about two hours to replace it by hydroxyl. The fused mass, after reaching the state in the experiment above described, must be stirred constantly to prevent charring. It finally turns deep-brown and becomes liquid, the change from the white, pasty mass to the semi-liquid condition being indicative of the complete replacement of the sulphonic acid group by hydroxyl. As soon as the mass assumed a liquid condition the heating was discontinued and the melt allowed to cool. It was then dissolved in water and acidified with hydrochloric acid and the solution extracted with ether. On evaporating the ether extract a small quantity of heavy, dark-colored oil was obtained. It was evidently impure, but the quantity was not sufficient to permit of its purification. The aqueous solution of this oil reduced an ammoniacal solution of silver nitrate and also Fehling's solution, and it gave a green color with ferric chloride. This agrees for the color reactions given for homopyrocatechol (methyl-1-dihydroxy-3,4-benzene), but the evidence is not regarded as conclusive that the substance is homopyrocatechol. Homopyrocatechol[1] is described as a brown syrup which, if distilled under diminished pressure, can be purified and made to solidify to a white mass, which melts at 49° to 50° and boils at 250° to 252°. It can be obtained in this condition only with great difficulty, and is generally obtained as a brown oil and recognized by its color reactions.

[1] Compt. rend., **115**, 234; **116**, 104; **118**, 809; **114**, 1543; Ber. d. chem. Ges., **10**, 210 J. Chem. Soc., **55**, 90; Ber. d. chem. Ges., **25**, 3533.

Paramethoxymetatoluenesulphone Chloride. — The sodium salt of paramethoxymetatoluenesulphonic acid was dried at 120°, finely powdered, and placed in a porcelain dish. To this salt an equal weight of phosphorus pentachloride was added and the mixture rubbed with a pestle. In a short time action took place and the mass turned to a light-yellow, oily material which, on cooling, became solid. It was then washed with water and a portion dissolved in benzene, from which it crystallized in light-yellow plates. It is soluble in ether and acetone. From the latter solvent perfectly colorless, transparent plates can be obtained if the solution is evaporated slowly in a vacuum-desiccator. These plates melt at 83°.5 to 84°. The same specimen, after it was allowed to cool, again melted at the same point.

0.1852 gram substance gave 0.1199 gram AgCl, or 0.02966 gram Cl.

	Calculated for $C_6H_3(CH_3)(SO_2Cl)(OCH_3)$	Found.
Cl	16.06	16.02

Paramethoxymetatoluenesulphonamide. — The chloride obtained as above described was finely powdered and 50 grams of it were placed in a beaker containing about 300 cc. strong ammonia and 200 cc. water. No immediate action was observed to take place, but on allowing the mixture to stand over night the mass at the bottom of the beaker changed from white to a dark-yellow color. This yellow mass was removed and crystallized from boiling water, from which it separated in needles which melted at 180° to 181°. It is insoluble in cold water, and soluble with great difficulty in boiling water. It is easily soluble in hot alcohol, which is the best solvent for its purification. From alcohol it separates in white needles. The ammoniacal solution was evaporated to dryness, and on the addition of cold water nearly the entire residue went into solution, showing that the amide is practically insoluble in ammonia.

0.2073 gram substance gave 0.2415 gram $BaSO_4$.

0.219 gram substance gave 0.2516 gram $BaSO_4$.
0.2835 gram substance gave 0.0205464 gram N.

	Calculated for $C_6H_3(CH_3)(OCH_3)-SO_2NH_2$.	Found. I.	II.	III.
S	15.92	15.98	15.77	....
N	6.96	....	....	7.21

Preparation of Paramethoxymetasulphaminebenzoic Acid.

In a long-necked balloon flask, of 3 liters capacity, 180 grams of potassium permanganate were placed and 2 liters of water added. To this solution 50 grams of paramethoxymetatoluenesulphonamide were added, the flask provided with a return-condenser, placed in a water-bath, and heated till the potassium permanganate was completely reduced. By this treatment it was expected that the methyl group would be oxidized to carboxyl.

When the purple color had entirely disappeared, the manganese hydroxide was filtered off and thoroughly washed with hot water. Strong hydrochloric acid was then added to the filtrate, and white needles separated. In order to remove any unoxidized amide, the material thus obtained was dissolved in dilute sodium carbonate in which the amide is insoluble. On addition of hydrochloric acid to the solution, the free acid again separated and was then crystallized from boiling water, in which it is sparingly soluble. Thus obtained, it melted at 252° to 277°, and repeated recrystallizations from water did not give a pure product. It was then dissolved in boiling absolute alcohol and obtained from this in a pure condition. Thus purified, it melted at 276° to 277°. At 274° there was a slight change in color, but no evidence of melting was observed on keeping the temperature at that point for some time. From alcohol both needles and plates were obtained from the same solution, but the melting-point of each indicated that they were identical except in crystal form. As a result of several experiments, it is believed that when the temperature of the water-bath, in which the flask is placed during the oxidation process, is not raised above 85° the yield

of the oxidation-product is greater than when the water in the bath is allowed to boil constantly. Almost a quantitative yield was obtained by slow oxidation at 85°, whereas, when the temperature was raised to about 100°, the quantity obtained was less than half of the theoretical.

0.2968 gram acid gave 0.0186 gram N.

0.3055 gram acid gave 0.019177 gram N.

0.2521 gram acid gave 0.2554 gram $BaSO_4$.

0.2802 gram acid gave 0.2838 gram $BaSO_4$.

0.2026 gram acid gave 0.3062 gram CO_2 and 0.0733 gram H_2O.

	Calculated for $C_6H_3(COOH)(SO_2NH_2)(OCH_3)$.	Found. I.	II.	III.	IV.	V.
C	41.56	41.21	....	....	....	....
H	3.89	4.02	....	....	....	....
N	6.06	....	6.27	6.28	....	....
S	13.85	....	....	....	13.91	13.97

Sodium Salt, $C_6H_3(COONa)(SO_2NH_2)(OCH_3) + 3H_2O$.—This salt separates from water in needles which have a slight cream color, but are transparent. The salt is insoluble in strong hot alcohol.

0.2364 gram salt lost, at 160°, 0.0372 gram H_2O and gave 0.0557 gram Na_2SO_4, or 0.01803 gram Na.

0.2623 gram salt lost, at 160°, 0.0414 gram H_2O and gave 0.062 gram Na_2SO_4, or 0.02008 gram Na.

	Calculated for $C_6H_3(COONa)(SO_2NH_2)(OCH_3) + 3H_2O$.	Found. I.	II.
H_2O	15.95	15.74	15.79
Na	7.64	7.62	7.65

Potassium Salt, $C_6H_3(COOK)(SO_2NH_2)(OCH_3) + 1\frac{1}{2}H_2O$.—The potassium salt crystallizes from water in extremely fine, almost colorless,

needles. It is very soluble in water and good crystals are obtained with difficulty. It is insoluble in cold alcohol.

0.3046 gram salt lost, at 210°, 0.0276 gram H_2O and gave 0.0889 gram K_2SO_4, or 0.03985 gram K.

0.2886 gram salt lost, at 210°, 0.0263 gram H_2O and gave 0.0842 gram K_2SO_4, or 0.0377 gram K.

	Calculated for $C_6H_3(COOK)(SO_2NH_2)(OCH_3) + 1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	9.12	9.06	9.11
K	13.18	13.08	13.08

Calcium Salt, $\left(C_6H_3(COO)(SO_2NH_2)(OCH_3)\right)_2Ca + 5H_2O$.—This forms white, glistening needles, arranged in clusters. It can be exposed to the air without losing its water. It is insoluble in cold or hot strong alcohol.

0.2195 gram salt lost, at 235°, 0.0335 gram H_2O and gave 0.0497 gram $CaSO_4$, or 0.01461 gram Ca.

0.2245 gram salt lost, at 235°, 0.0341 gram H_2O and gave 0.0503 gram $CaSO_4$, or 0.01479 gram Ca.

	Calculated for $\left(C_6H_3(COO)(SO_2NH_2)(OCH_3)\right)_2Ca + 5H_2O$.	Found. I.	II.
H_2O	15.25	15.27	15.19
Ca	6.77	6.65	6.59

Barium Salt, $\left(C_6H_3(COO)(SO_2NH_2)(OCH_3)\right)_2Ba + 4\frac{1}{2}H_2O$.—This appears in the form of colorless needles, radiating from a center and in form resembling a chestnut burr. It is almost insoluble in alcohol, but easily soluble in cold water. In order to dehydrate the salt completely it was necessary to heat it for a long time at 245°. It decomposes at about 255°.

0.3400 gram salt lost, at 245°, 0.041 gram H_2O and gave 0.1174 gram $BaSO_4$, or 0.069 gram Ba.

0.3314 gram salt lost, at 245°, 0.0396 gram H_2O and gave 0.1154 gram $BaSO_4$, or 0.0679 gram Ba.

	Calculated for $\left(C_6H_3\begin{matrix}COO\\SO_2NH_2\\OCH_3\end{matrix}\right)_2Ba + 4\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	11.93	12.06	11.95
Ba	20.29	20.33	20.49

Magnesium Salt, $\left(C_6H_3\begin{matrix}COO\\SO_2NH_2\\OCH_3\end{matrix}\right)_2Mg + 6H_2O$. — This separates from water in fine, silky needles. These needles, when removed from the solution for the purpose of drying, were accidentally placed in a warm place and they went into solution. From this concentrated solution colorless crystals, which have the appearance of thick, triclinic prisms, separated. These crystals were remarkable for their iridescence. It was noticed that from the same solution both needles and prisms would separate, only a few prisms crystallizing when the solution was dilute and the needles compact. Analysis of the prismatic crystals gave the following result:

0.2901 gram salt lost, at 225°, 0.0521 gram H_2O and gave 0.0201 gram MgO, or 0.01207 gram Mg.

0.2328 gram salt lost, at 235°, 0.0428 gram H_2O.

0.2533 gram salt gave 0.0172 gram MgO, or 0.01033 gram Mg.

It was found necessary to add fine ammonium carbonate in order to get rid of the sulphonic acid residue. Without this addition the results for magnesium were high, showing that magnesium sulphate had probably been formed.

	Calculated for $\left(C_6H_3\begin{matrix}COO\\SO_2NH_2\\OCH_3\end{matrix}\right)_2Mg + 6H_2O$.	Found. I.	II.
H_2O	18.24	17.96	18.34
Mg	4.05	4.16	4.08

Analysis of the air-dried acicular crystals indicated that they contained 10.5 molecules of water. Both kinds of crystals were exposed to the air without losing their water of crystallization.

Fusion of Paramethoxymetasulphaminebenzoic Acid with Potassium Hydroxide.

About 40 grams of potassium hydroxide were heated with a little water in a silver dish until the alkali was dissolved. About 5 grams of the paramethoxymetasulphaminebenzoic acid were then added. The addition of the acid is most conveniently made by first dissolving it in aqueous potassium hydroxide and then adding the solution slowly. The fusion was carried on for about twenty minutes, care being taken to avoid too high a temperature in order that the compound might not be entirely broken down. The mass was then dissolved in water and acidified with hydrochloric acid. No odor of sulphur dioxide was perceptible, showing that the group SO_2NH_2 had not been replaced by hydroxyl. On standing for some time in a cool place, white needles separated. The crystals were arranged in radiating clusters and had a more blunt, prism-like appearance than the corresponding methoxy compound. The compound crystallizes well from alcohol, and is more soluble in water than the paramethoxymetasulphaminebenzoic acid. Its melting-point is 258°, and it decomposes at about 265°. Analysis shows it to be parahydroxymetasulphaminebenzoic acid.

0.3049 gram acid gave 0.01999 gram N.

0.3065 gram acid gave 0.02033 gram N.

0.2022 gram acid gave 0.0528 gram H_2O, or 0.00587 gram H, and 0.285 gram CO_2, or 0.0777 gram C.

0.2413 gram acid gave 0.2605 gram $BaSO_4$, or 0.0358 gram S.

	Calculated for $C_6H_3\begin{cases}COOH\\SO_2NH_2\\OH\end{cases}$.	Found. I.	II.	III.	IV.
C	38.76	....	....	....	38.44
H	3.22	....	....	....	2.90
N	6.45	6.56	6.63	....	....
S	14.75	....	....	14.83	....

Sodium Salt, $C_6H_3\begin{cases}COONa\\SO_2NH_2\\OH\end{cases} + 4H_2O$. — This salt forms

white, radiating needles which are very soluble in water but insoluble in boiling, strong alcohol.

0.2203 gram salt lost, at 170°, 0.0506 gram H_2O and gave 0.0499 gram Na_2SO_4, or 0.01616 gram Na.

	Calculated for $C_6H_3(COONa)(SO_2NH_2)(OH) + 4H_2O$.	Found.
H_2O	23.15	22.97
Na	7.40	7.34

Barium Salt, $\left(C_6H_3(COO)(SO_2NH_2)(OH)\right)_2Ba + 6\frac{1}{2}H_2O$.—This separated in white tufts, which are easily soluble in water and insoluble in boiling alcohol.

0.2381 gram salt lost, at 240°, 0.0403 gram H_2O and gave 0.0812 gram $BaSO_4$, or 0.0478 gram Ba.

	Calculated for $\left(C_6H_3(COO)(SO_2NH_2)(OH)\right)_2Ba + 6\frac{1}{2}H_2O$.	Found.
H_2O	17.03	16.93
Ba	20.01	20.06

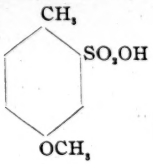
Further Action of Potassium Hydroxide on Paramethoxymetasulphaminebenzoic Acid.

It was found in a previous experiment that the methoxy group in the methoxysulphamine acid could be replaced by hydroxyl without the removal of the sulphamine group. In order to test the further action of potassium hydroxide on this acid, 20 grams of potassium hydroxide were placed, together with a little water, in a silver dish and melted. To this mass about 3 grams of the methoxysulphamine acid were gradually added, and the mass fused, at a high temperature, for about two hours. On dissolving the mass, and acidifying it with hydrochloric acid, sulphur dioxide was given off in abundance. The acidified solution was then extracted with ether, the ether evaporated, and a dark, semi-crystalline mass obtained. This was dissolved in alcohol, from which it separa-

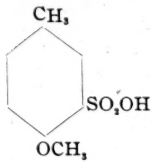
ted in yellow crystals, which melted at 187° to 192°. This material reduced an ammoniacal solution of silver nitrate, but had no effect on Fehling's solution. Ferric chloride added to an aqueous solution of the substance produced a blue-green color, which turned red on the addition of sodium carbonate. This is clear evidence that the substance is protocatechuic acid, and is, therefore, confirmatory evidence that the sulphamine group is in the meta position.

Discussion of the Evidence which Shows that the Sulphonic Acid Group in Paramethoxymetatoluenesulphonic Acid is in the Meta Position.

There are two possibilities for the entrance of a single SO_3OH group, in paramethoxytoluene, which may be represented by formulas I. and II.:



I.



II.

The first, by the replacement of the methoxy and sulphamine groups by hydroxyl, by fusion with potassium hydroxide, should yield methyl-1-dihydroxy-2,4-benzene; the second, by similar treatment, should give homopyrocatechol or methyl-1-dihydroxy-3,4-benzene. It is believed that the latter product was obtained, but the evidence on this point is not conclusive.

By treatment with phosphorus pentachloride, the sodium salt of the sulphonic acid (I.) should yield a chloride, $C_6H_3\begin{cases}CH_3\\SO_2Cl(o)\\OCH_3(p)\end{cases}$, and this, on treatment with ammonia, should give the amide, $C_6H_3\begin{cases}CH_3\\SO_2NH_2(o)\\OCH_3(p)\end{cases}$. On oxidizing this amide

with potassium permanganate a sulphinide would be obtained having the formula $C_6H_3\begin{cases}CO\\SO_2\\OCH_3\end{cases}>NH$. All these compounds were made by Parks,[1] working in this laboratory. The compounds which Parks obtained agree in no respect with those obtained by the writer. The chloride made by Parks is an oil; the amide is composed of white needles and melts at 150°, and the sulphinide, of needles which melt at 271°.

Metcalf,[2] working in this laboratory, by diazotizing paratoluidinemetasulphonic acid, decomposing the product with methyl alcohol, and then treating the sodium salt of the resulting compound with phosphorus pentachloride, obtained a chloride which had the formula $C_6H_3\begin{cases}CH_3\\SO_2Cl(m)\\OCH_3(p)\end{cases}$. From this chloride he obtained the amide $C_6H_3\begin{cases}CH_3\\SO_2NH_2(m)\\OCH_3(p)\end{cases}$, and on oxidizing this a compound, which he took to be $C_6H_3\begin{cases}COOH\\SO_2NH_2(m)\\OCH_3(p)\end{cases}$, although it was impure, as indicated by its melting-point.

The compounds the writer obtained agree with those which Metcalf made. In addition to this the writer, by fusing the acid, $C_6H_3\begin{cases}COOH\\SO_2NH_2(m)\\OCH_3(p)\end{cases}$, with potassium hydroxide obtained protocatechuic acid, $C_6H_3\begin{cases}COOH\\OH(m)\\OH(p)\end{cases}$. All these facts go to show that the group SO_2OH entered in the meta position, and

[1] This JOURNAL, 15, 320.
[2] *Ibid.*, 15, 301.

that the sulphonic acid first formed is that indicated by formula II, or paramethoxymetatoluenesulphonic acid.

Summary of Results.

1. When paradiazotoluene sulphate is decomposed, at the ordinary pressure, with methyl alcohol in the presence of the compounds formed during the diazotizing process, both the methoxy and hydrogen reactions take place; the latter, however, to a very small extent.

2. When paramethoxytoluene is treated with sulphuric acid but one sulphuric acid residue enters the compound, and the sulphonic acid group takes the meta position.

3. When paramethoxymetatoluenesulphonic acid is fused with potassium hydroxide at a comparatively low temperature, potassium parahydroxymetatoluenesulphonate is formed; at higher temperatures homopyrocatechol appears to be formed.

4. When oxidized with potassium permanganate, paramethoxymetatoluenesulphonamide yields paramethoxymetasulphaminebenzoic acid.

5. When paramethoxymetasulphaminebenzoic acid is cautiously fused with potassium hydroxide parahydroxymetasulphaminebenzoic acid is obtained; on prolonged fusion at a high temperature, protocatechuic acid is formed.

Contributions from the New York Agricultural Experiment Station.

VI.—CHEMICAL CHANGES IN CHEESE-RIPENING AS AFFECTED BY DIFFERENT CONDITIONS.

By Lucius L. Van Slyke and Edwin B. Hart.

The object of this article is to present the results of our study relating to some of the more prominent conditions that influence the chemical changes taking place in the nitrogen compounds of cheese during the ripening process. It is well known that, during the cheese-making process, chemical changes soon begin in the freshly coagulated curd or paracasein formed when milk casein is acted upon by rennet. The same cheese examined at intervals is found to show quite

marked variations in the character of its nitrogen compounds. Cheeses made from the same milk under the same conditions of manufacture and subjected to different conditions during the ripening process show a difference in chemical composition. Cheeses manufactured under different conditions and ripened under uniform conditions may vary in the character of their nitrogen compounds. It has seemed to us desirable that a somewhat comprehensive study should be made of the changes actually found in the nitrogen compounds of cheese, using in the work only cheeses made and ripened under known, controlled conditions. The results presented in this article by no means exhaust the subject, our intention being to study first only some of the more prominent factors, such as time, temperature, moisture, salt, rennet, and acid.

The chief proteid of curd, freshly coagulated by rennet, consists, under usual conditions, of a compound called paracasein, in some respects resembling milk-casein, in other respects differing from it in a marked degree. The exact chemical relation of these two compounds has not yet been learned. In the usual methods of cheese-making the milk sugar, acted on by certain organisms, begins to form lactic acid early in the process, and this acid, as rapidly as formed, combines chemically with paracasein to form a compound called paracasein monolactate. Many of the peculiar properties of curd are believed to be due to the presence of this paracasein monolactate, such as the ability to form fine strings on a hot iron, the changes in appearance, plasticity and texture, and, perhaps, the shrinking. It is also probable that paracasein monolactate forms the real starting-point of cheese ripening, or, stated another way, that we must have paracasein monolactate present before we can have formed such compounds as caseoses, peptones, and amides. Starting with the casein of milk, we have in cheese-curd and ripening cheese the following nitrogen compounds formed in something like the following order: Paracasein, paracasein monolactate, paranuclein, caseoses, peptones, amido compounds, and ammonia compounds. The amounts of these different compounds and classes of compounds, and their relations to one another, we shall study in some detail in the following pages.

The Relation of Time to the Chemical Changes of Cheese-Ripening.

As we shall point out later, the effect of time as a factor in cheese-ripening is modified by a variety of conditions. For purpose of illustration, we will here give averages of the results obtained under various conditions. Each analysis represents averages of the results obtained with 24 different cheeses.

Table I.—Showing Effect of Time on Cheese-ripening.

	Nitrogen, expressed as percentage of nitrogen in cheese, in form of						
Age of cheese.	Paracasein monolactate.	Water-soluble nitrogen comp'ds.	Paranuclein.	Caseoses.	Peptones.	Amides.	Ammonia.
Months.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per c't.
1½	20.18	21.44	2.06	3.15	3.84	9.88	1.56
3	27.26	30.98	4.45	4.56	4.65	14.36	2.45
6	27.55	36.15	3.57	4.92	4.22	19.96	3.52
9	24.14	43.45	4.02	4.59	3.56	26.53	4.74
12	19.04	44.75	3.52	4.16	3.95	28.38	5.41
18	12.65	47.25	3.40	3.88	2.57	30.46	6.62

The data embodied in this table suggest the following statements:

(1) The total amount of nitrogen in the form of water-soluble compounds increases as the cheese gains in age. This increase is more rapid in the early stages of ripening. Of the total amount of water-soluble nitrogen compounds formed in the cheese during eighteen months, 45.4 per cent was formed in the first month and a half; 65.5 per cent in the first three months; 76.5 per cent in the first six months; and 92 per cent in the first nine months, or one-half the entire period covered by the study.

(2) The nitrogen in the form of paracasein monolactate appears to increase for six months and then gradually decrease. However, these data are not calculated to show the variations of this compound to advantage, since we have learned from other work of ours that paracasein monolactate commonly ap-

pears at its maximum quantity in fresh cheese and is very largely changed into other forms in the course of a few weeks, the rapidity of its appearance and disappearance being dependent upon such conditions as the acidity of the cheese, the temperature of the curing room, etc.

(3) The nitrogen in the form of paranuclein, caseoses, and peptones varies comparatively little, but there is a general tendency to a decrease in amount with increase of age in cheese.

(4) The amido compounds increase with comparative rapidity during the early stages of ripening. The increase continued during the whole period of study but at a less rapid rate. Thus, of the entire amount of amido compounds formed during eighteen months, 87 per cent was found at the end of nine months, and about 33 per cent at the end of one month and a half.

(5) The ammonia in cheese does not commonly reach an appreciable quantity until cheese is about a month old, after which it increases quite regularly. It forms less slowly in the later than in the early stages of ripening. Considerably over half the ammonia was formed in the first six months.

The Relation of Temperature to the Chemical Changes of Cheese-ripening.

In general, we find in every individual cheese that temperature exerts a marked influence upon the changes taking place in the nitrogen compounds. The effect of temperature is modified by other conditions. In the table on the following page we consider, along with the temperature, the time factor.

Summarizing our results, we find that, other conditions being uniform, (*a*) the water-soluble nitrogen compounds in cheese increase on an average very closely in proportion to increase of temperature; (*b*) from the average of our results, there is an increase of 0.5 per cent of water-soluble nitrogen compounds for an increase of 1° of temperature between the limits of 32° F. and 70° F.; (*c*) the amido compounds and ammonia are formed in the cheese more abundantly at higher

Table II.—Showing Effect of Temperature on Cheese-ripening.

Temperature of curing-room. Degrees F.	Form of nitrogen compound.	Nitrogen, expressed as percentage of nitrogen, in cheese. One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
32	Total water-soluble	12.80	18.64	23.06	32.66	34.02	36.75
55	" "	20.56	31.46	36.09	43.91	45.09	49.40
60	" "	23.14	33.69	39.97	46.89	48.62	50.16
70	" "	29.24	40.13	45.50	50.34	51.25	52.67
32	Paracasein monolactate	20.58	43.14	36.55	43.00	34.48	21.37
55	" "	33.01	33.66	35.10	25.61	19.26	19.45
60	" "	13.89	18.81	19.94	16.15	12.32	9.45
70	" "	13.24	13.45	18.62	11.83	10.10	7.86
32	Paranuclein	1.27	4.05	3.44	4.47	4.15	4.12
55	"	2.39	5.34	4.25	4.27	3.64	3.68
60	"	2.54	4.71	3.90	4.23	3.59	4.73
70	"	2.03	3.71	2.68	3.13	2.45	2.60
32	Caseoses	1.05	2.97	5.24	4.29	4.17	5.06
55	"	4.08	4.50	5.03	4.76	4.73	4.27
60	"	3.44	6.14	6.03	5.07	3.68	3.00
70	"	4.07	4.63	3.37	4.24	4.12	3.20
32	Peptones	1.30	2.23	4.53	4.36	4.53	4.17
55	"	3.90	4.95	3.99	3.10	3.72	2.84
60	"	3.33	5.99	4.70	3.44	4.03	1.80
70	"	6.81	5.45	3.67	3.33	3.51	1.50
32	Amides	4.82	6.36	8.70	17.55	18.73	19.44
55	"	8.69	14.33	19.55	27.05	29.00	31.66
60	"	12.16	14.55	21.39	28.84	31.14	33.54
70	"	13.86	22.20	30.80	32.68	34.65	37.19
32	Ammonia	0.61	0.61	1.21	1.91	2.14	3.98
55	"	1.50	2.42	3.30	4.69	5.57	6.95
60	"	1.67	2.54	3.89	5.43	6.12	7.35
70	"	2.47	4.22	5.71	6.91	7.49	8.19

temperatures and accumulate in the cheese, while the other water-soluble compounds of nitrogen and also paracasein monolactate do not appear to be regularly influenced by temperature in the early stages of ripening, but after some months they decrease in quantity with increase of temperature.

The Relation of Moisture to the Chemical Changes of Cheese-ripening.

In order to study the effect of moisture in cheese upon the chemical changes taking place in the nitrogen compounds, two sets of cheeses were made for comparison, four different cheeses in each set being made under parallel conditions. The cheeses designated as 42 were covered with melted paraffin, in order to retard the evaporation of water from the cheese. Those designated as 39 were left in the usual condition. These cheeses were all kept in the same curing-room at a temperature of 55° F. (See Table III.)

Comparing the results presented in Table III. we notice the following points of difference:

(1) The cheeses covered with paraffin had somewhat less water when made but the others lost water more rapidly, so that at the end of three months their water-content was about the same. After this the paraffined cheese contained considerably more water, the difference increasing with age, until at the end of 12 months it was over 4.5 pounds per 100 pounds of cheese.

(2) During the first three months the amount of water-soluble nitrogen compounds was about the same in both kinds of cheese, but from this point the amount increased more rapidly in the cheeses covered with paraffin, that is, in those cheeses containing more moisture. The difference becomes more marked at each succeeding analysis.

(3) After six months the paracasein monolactate disappears much more rapidly in the cheeses containing more moisture, the difference increasing up to twelve months.

The Relation of Salt in Cheese to the Chemical Changes of Cheese-ripening.

In Bulletin No. 203 of this Station, page 241, attention is

Table III.—Showing Effect of Moisture in Cheese on Cheese-ripening.

No. of cheese.	Form of nitrogen compound.	Nitrogen expressed as percentage of nitrogen in cheese. One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
39	Total water-soluble	17.32	27.09	31.76	39.09	39.80	42.77
42	" "	17.14	27.40	36.41	46.59	54.52	56.76
39	Paracasein monolactate	24.89	41.59	35.43	28.81	21.70	13.72
42	" "	21.17	30.42	49.29	20.16	9.81	5.30
39	Paranuclein	2.70	5.32	4.77	4.20	3.79	4.10
42	"	0.87	4.35	4.45	4.89	8.01	7.90
39	Caseoses	2.99	5.80	4.24	4.41	4.19	4.26
42	"	3.58	3.64	5.38	5.06	4.32	4.70
39	Peptones	2.12	4.09	3.75	3.57	3.97	1.95
42	"	4.49	4.80	6.19	4.00	4.43	3.20
39	Amides	7.50	9.79	16.00	21.65	22.89	26.73
42	"	7.22	12.59	17.12	26.03	29.44	29.00
39	Ammonia	1.34	2.15	3.04	4.17	4.53	5.72
42	"	0.98	1.99	4.26	6.52	8.27	12.16
39	Water	36.40	35.27	32.41	27.86	28.02	27.75
42	"	35.96	35.00	33.37	33.24	32.66	32.10

Table IV.—Showing Effect of Salt on Cheese-ripening.

Amount of salt used for 1000 lbs. of milk.	Form of nitrogen compound.	Nitrogen expressed as percentage of nitrogen in cheese.					
		One and a half months.	Three months.	Six months.	Nine months.	Twelve months.	Eighteen months.
Lbs.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
0	Total water-soluble	23.42	34.26	40.52	49.10	51.38	53.96
1.5	" "	21.80	32.10	37.67	44.13	45.88	50.73
2.5	" "	21.67	29.92	34.73	42.93	43.52	44.65
5	" "	18.84	27.70	31.70	37.64	38.19	39.62
0	Paracasein monolactate	17.33	27.06	23.27	21.82	16.75	12.56
1.5	" "	20.86	28.43	26.16	22.38	17.98	12.61
2.5	" "	21.81	24.47	28.30	23.54	18.04	13.74
5	" "	20.73	29.02	32.49	28.81	23.41	11.71
0	Paranuclein	1.85	4.44	3.80	4.66	3.83	3.44
1.5	"	2.13	4.47	3.52	4.01	3.72	3.89
2.5	"	2.27	4.55	3.51	3.80	3.30	3.34
5	"	1.98	4.35	3.42	3.63	3.23	2.96
0	Caseoses	3.41	4.94	4.94	5.60	4.95	3.87
1.5	"	3.24	5.02	5.17	4.53	3.69	4.04
2.5	"	3.21	4.14	4.98	4.16	3.97	3.84
5	"	2.75	4.14	4.58	4.08	4.05	3.77
0	Peptones	4.86	5.02	4.84	3.47	4.13	2.69
1.5	"	3.50	5.16	4.29	3.54	4.87	3.40
2.5	"	4.20	4.02	4.02	3.97	3.98	2.07
5	"	2.91	4.42	3.74	3.25	2.81	2.14

Table IV.—Showing Effect of Salt on Cheese-ripening (Continued).

Amount of salt used for 1000 lbs. of milk. Lbs.	Form of nitrogen compounds.	Nitrogen expressed as percentage of nitrogen in cheese. One and a half months. Per cent.	Three months. Per cent.	Six months. Per cent.	Nine months. Per cent.	Twelve months. Per cent.	Eighteen months. Per cent.
0	Amides	10.22	15.86	22.18	28.89	32.19	35.09
1.5	"	10.46	14.77	20.13	27.31	29.33	32.36
2.5	"	9.78	13.83	19;20	26.72	27.61	29.57
5	"	8.82	12.97	17.34	23.21	24.40	24.81
0	Ammonia	1.67	2.96	4.64	6.54	7.77	8.89
1.5	"	1.67	2.53	3.69	4.69	5.36	7.04
2.5	"	1.51	2.36	3.13	4.30	4.54	5.83
5	"	1.41	2.03	2.64	3.43	3.61	4.70
0	Per cent water in cheese	39.27	38.22	35.60	35.22	34.09	30.96
1.5	" " " "	36.66	35.60	33.50	32.62	31.61	28.80
2.5	" " " "	35.69	34.43	32.31	31.54	30.99	27.68
5	" " " "	33.63	32.62	29.52	29.88	28.61	26.97
0	Per cent salt in cheese	0	0	0	0	0	0
1.5	" " " "	0.59	0.70	0.84	0.94	0.92	....
2.5	" " " "	0.82	1.20	1.15	1.26	1.27	....
5	" " " "	1.29	1.50	1.62	1.87	1.83	....

called to the fact that salt exerts a retarding influence upon the proteolytic action of enzymes in cheese. Since the results given there were secured with cheese made and kept in the presence of chloroform, it was desired to make a study of the influence of salt upon the ripening process in cheese normally made and kept under normal conditions. For the purpose of such a study, 4 different lots of cheese were made under normal conditions as nearly alike as possible, and salt was added to these in proportions varying as follows: No salt, 1.5, 2.5, and 5 pounds of salt for 1,000 pounds of milk. In Table IV. we give the averages of the different lots of cheeses.

We are to regard the salt in cheese as being in solution in the whey held by the cheese, practically forming a dilute brine. In common practice, cheesemakers add from 2 to 2.5 pounds of salt to the curd made from 1,000 pounds of milk. Cheese thus salted contains about 1 per cent of salt. Such cheese usually contains about 35 to 37 per cent of water. Consequently, under such conditions we should have approximately a 3 per cent brine. It is evident that in proportion as a cheese loses moisture by evaporation, the salt brine remaining becomes more concentrated with the advancing age of the cheese.

A study of the data contained in Table IV. enables us to make the following statements:

(1) The amount of salt retained in cheese is not proportional to the amount of salt added to the curd. Of necessity, a considerable proportion of the salt added to cheese curd passes into the whey.

(2) An increase of salt in cheese curd results in decreasing the amount of moisture held in cheese.

(3) An increase of salt in cheese was accompanied by a decrease in the amount of water-soluble nitrogen compounds and this was true through the whole eighteen months of the investigation. While this influence of salt is more noticeable in the case of the amido compounds and ammonia, it is clearly evident in the case of the paranuclein, caseoses, and peptones.

(4) The paracasein monolactate disappears less rapidly in the cheeses containing more salt.

It is readily seen from the results embodied in Table IV. that the rapidity of formation of water-soluble nitrogen compounds is decreased in the presence of increased amounts of salt in cheese. The question arises whether this is due directly to a retarding action of salt upon the agencies that cause cheese-ripening or to the effect of salt in decreasing the amount of moisture held in cheese. It is true that some of the observed differences in proteolysis can be accounted for by the difference in moisture-content noticed in the various cheeses. While this set of experiments does not clearly demonstrate that salt has in itself a direct retarding effect upon the cheese-ripening process, we have some results obtained with another experiment which indicate that salt has a retarding effect upon proteolysis in cheese. In some experiments made in another line of work, salt clearly exerted a retarding influence upon the formation of water-soluble nitrogen compounds. Then, again, some work carried on with milk, where there was no difference of water-content, indicates the same retarding action of salt.

The Relation of Varying Amounts of Rennet-Enzyme to the Chemical Changes of Cheese-ripening.

In Bulletin No. 54, page 267, are given the results of some experiments made in 1892 at this Station, when a comparison was made of the amount of water-soluble nitrogen formed in cheeses made with 3 and 9 ounces of rennet-extract per 1000 pounds of milk. Considerably larger amounts of soluble nitrogen were found when the larger amount of rennet was used. In 1899 some further experiments were made, using 3 and 6 ounces of Hansen's rennet-extract for 1000 pounds of milk. The cheeses were so made as to contain about the same amount of moisture.

The data embodied in Table V. show quite generally a greater increase of water-soluble nitrogen compounds in the cheese containing the larger amount of rennet.

If we examine the different classes of the water-soluble nitrogen compounds, we notice that the increase caused by increased use of rennet is more noticeable in the case of the

Table V.—Showing Effect of Different Amounts of Rennet upon Cheese-ripening.

Age of cheese.	Amount of rennet-extract used for 1,000 pounds of milk.	Percentage of water in cheese.	Nitrogen expressed as percentage of nitrogen in cheese in form of			
			Water-soluble nitrogen.	Paranuclein, caseoses, and peptones.	Amides.	Ammonia.
Months.	Ounces.		Per cent.	Per cent.	Per cent.	Per cent.
1	3	37.54	18.90	10.31	8.36	....
1	6	38.06	23.40	13.37	9.47	....
3	3	35.59	26.70	13.34	12.00	1.87
3	6	36.25	29.70	15.40	12.50	1.86
6	3	33.58	29.80	12.02	16.20	2.09
6	6	33.51	35.40	15.11	18.20	2.60
9	3	31.84	37.30	13.47	21.20	2.59
9	6	30.63	35.50	13.00	20.00	2.50
12	3	28.13	38.00	12.05	22.10	4.10
12	6	29.98	42.40	14.38	24.00	3.60
15	3	26.73	39.10	12.05	22.90	4.53
15	6	25.97	43.60	13.19	25.50	4.31
24	3	24.76	42.70	12.30	25.10	5.06
24	6	23.33	48.50	14.54	28.50	5.84

paranuclein, caseoses, and peptones than in the case of the amides and ammonia, especially during the first six or nine months. After a year, the tendency is for a greater difference among the amides caused by increased use of rennet than between the other soluble nitrogen compounds.

These results are in harmony with some work done by Babcock, Russell, and Vivian,[1] who used 3, 9, 12, 18, and 24 ounces of rennet-extract per 1,000 pounds of milk, and made analyses of the cheese at one, two, and six months. In this period of time they found that, while there was a constant increase in the amount of total water-soluble nitrogen compounds when there was an increase in the amount of rennet used, this increase came mostly to the caseoses and peptones, the amides and ammonia remaining quite constant.

[1] Ann. Rep., Wis. Expt. Sta., 17, 102 (1900).

Summary and Discussion of Results.

Reviewing briefly the results that have been presented in the preceding pages, we have found that different conditions affect the chemical changes in the nitrogen compounds of cheese as follows:

(1) *Time.*—The formation of water-soluble nitrogen compounds increases as cheese ages, other conditions being uniform. The rate of increase is, however, not uniform, since it is much more rapid in the early, than in the succeeding, stages of ripening.

(2) *Temperature.*—The amount of soluble nitrogen compounds increases, on an average, quite closely in proportion to increase of temperature, when other conditions are uniform.

(3) *Moisture.*—Other conditions being alike, there is formed a larger amount of water-soluble nitrogen compounds in cheese containing more moisture than in cheese containing less moisture.

(4) *Size.*—Cheeses of large size usually form water-soluble compounds more rapidly than smaller cheeses under the same conditions, because large cheeses lose their moisture less rapidly and after the early period of ripening have a higher water-content.

(5) *Salt.*—Cheese containing more salt forms water-soluble nitrogen compounds more slowly than cheese containing less salt. This appears to be due, in part, to the direct action of salt in retarding the activity of one or more of the ripening agents and, in part, to the tendency of the salt to reduce the moisture-content of the cheese.

(6) *Rennet.*—The use of increased amounts of rennet-extract in cheese-making, other conditions being uniform, results in producing increased quantities of water-soluble nitrogen compounds in a given period of time, especially such compounds as paranuclein, caseoses, and peptones.

(7) *Acid* appears to be essential to the formation of water-soluble nitrogen compounds in normal cheese-ripening, but the exact influence of varying quantities of acid upon the

chemical changes of the ripening process has not yet been fully studied.

Transient and Cumulative Products in Cheese-ripening.

In studying the influence of various conditions upon the chemical changes of the nitrogen compounds in the normal cheese-ripening process, we have noticed that the compounds grouped under the names paracasein, caseoses, and peptones, usually vary within comparatively narrow limits and do not appear to accumulate in the cheese in constantly increasing quantities. These compounds do not appear to show much definite regularity in the amounts formed under different conditions. On the other hand, amido compounds and ammonia accumulate in increasing amounts from the early age of the cheese during the whole process of normal ripening. The difference in the apparent behavior of these different classes of nitrogen compounds is most readily explained by regarding the compounds first formed in cheese-ripening as intermediate transient-products. Thus we find paranuclein, caseoses, and peptones present in the earliest stage of cheese-ripening, and they show a tendency to increase somewhat for a period of time and then decrease. Just what the chemical relation of these compounds is to paracasein, or to paracasein monolactate, we are unable to say. It is probable that the molecule of the proteid compound first splits into paranuclein and caseoses or some closely related compounds, and from one or both these classes of compounds are formed peptones. Whatever may be the precise chemical relation and order of formation, the point we wish to keep in mind is that the amounts of these compounds do not increase regularly or accumulate continuously in the cheese. The extent to which any accumulation occurs in these transient stages depends upon the conditions of ripening. For example, at low temperatures, the transient nitrogen products formed appear to pass into other forms less rapidly than at higher temperatures and they tend to accumulate to some extent. This can be shown by comparing the results secured with cheeses ripened at 32° F. and 70° F. These data are taken from Table II. :

Age of cheese.	Percentage of nitrogen in form of paranuclein in cheese at		Percentage of nitrogen in form of caseoses in cheese at		Percentage of nitrogen in form of peptones in cheese at	
	32° F.	70° F.	32° F.	70° F.	32° F.	70° F.
Months.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.5	1.27	2.03	1.05	4.07	1.30	6.81
3	4.05	3.71	2.97	4.63	2.23	5.45
6	3.44	2.68	5.24	3.37	4.53	3.67
9	4.47	3.13	4.29	4.24	4.36	3.33
12	4.15	2.45	4.17	4.12	4.53	3.51
18	4.12	2.60	5.06	3.20	4.17	1.50

Now, quite different from the behavior of these compounds is that of amido compounds, which appear beyond question to result from the proteolysis of peptones, and of ammonia, which is formed from the decomposition of amides. Ammonia is an end-product and the amido compounds are end-products to a considerable extent in cheese normally ripened. They therefore accumulate in increasing quantities under all conditions that favor their formation.

Influence of Products of Proteolysis on the Cheese-ripening Process.

Attention has been called to the fact that chemical changes in the nitrogen compounds of cheese take place much more rapidly in the early stages of ripening than later. In our work we found that in the first three months of the eighteen-month period of study, over 65 per cent of the nitrogen was changed into the form of water-soluble compounds. How can we explain this observed fact that the rate of chemical change, as measured by the formation of water-soluble nitrogen compounds, decreases as the age of cheese increases? The most obvious explanation is associated with the generally observed fact that in fermentation changes the products of the process weaken the action of the ferment, often inhibiting it altogether. In cheese we have an accumulation of fermentation-products in the form of water-soluble nitrogen compounds and, apparently, they serve to diminish the action of the agents that cause the changes.

In this connection it is interesting to notice that the end-products, the amides, and ammonia appear to exert a stronger influence than do the other soluble nitrogen compounds in de-

creasing the action of the ripening agents. This is indicated by the following data taken from Table I.:

Age of cheese. Months.	Percentage of nitrogen in form of paranuclein, caseoses, and peptones.	Percentage of nitrogen in form of amides and ammonia.	Monthly average rate of increase of soluble nitrogen compounds for 100 lbs. of nitrogen in cheese. Lbs.
1.5	9.05	11.44	15.0
3	13.66	16.81	6.3
6	12.71	23.48	2.1
9	12.17	31.27	2.4
12	11.63	33.79	0.4
18	....	37.00	0.4

Thus, it is seen that the first-formed products of cheese-ripening, paranuclein, caseoses, and peptones, remain fairly uniform, while the amides and ammonia continuously increase.

Why Moisture Influences the Cheese-ripening Process.

We have seen that an increased moisture-content in cheese favors more active chemical changes in the process of ripening. This may be due to one or both of two effects. First, moisture in itself may favor the activity of the ripening ferments. It is well known that moisture is necessary for the action of ferments and that increase of moisture above a certain amount increases their action. Second, the presence of increased amounts of moisture serves to dilute the fermentation-products and to that extent to counteract their unfavorable effect.

In ordinary cheese-ripening there is a constant loss of moisture, and this serves to make more concentrated the fermentation-products which are increasing at the same time the moisture is decreasing. Accordingly, after three to six months, difference in moisture appears from the results of our work to exert a more marked influence upon the increased formation of soluble nitrogen compounds than in the early stages of ripening.

The Character of the Action of Rennet-Extract.

In Bulletin No. 233 of this Station the work of others has

been confirmed in showing that the active constituent of rennet is a peptic ferment and that the part performed in cheese-ripening by rennet-extract is a peptic digestion, in which the chemical changes are largely confined to the conversion of paracasein monolactate into paranuclein, caseoses, and peptones, only small amounts of amides being formed.

The Relation of Acid in Cheese to Cheese-ripening.

In Bulletin No. 203, page 240, of this Station, we called attention to the fact that presence of acid in cheese favors the action of enzymes in the cheese-ripening process. In this JOURNAL, **28**, No. 6, Dec., 1902, it was shown that acid performs a specific function in the cheese-making process, uniting with paracasein to form paracasein monolactate. It was also shown that paracasein monolactate appears to form the real starting-point of the cheese-ripening process, since we have been unable to obtain soluble nitrogen compounds to any extent without the presence of paracasein monolactate and since this compound decreases in amount as soluble nitrogen compounds increase.

From our work previously done, it appears that acid in cheese is a prerequisite for its ripening. Additional work is required to show the specific influence of different amounts of acid upon the cheese-ripening process.

NOTE ON THE BUDDE EFFECT WITH REFERENCE TO BROMINE.

BY B. PALMER CALDWELL.

In the course of some investigations attempting to solve the problem of the increased chemical activity of chlorine in sunlight, we were led to try a few experiments with bromine. As the work was interrupted in its preliminary stage, no conclusions were reached. In the meantime, several papers on the same general subject by J. W. Mellor and Edward John Russell have appeared in the Journal of the London Chemical Society (1902). As these authors in their work have devoted themselves to experiments with chlorine alone,

we have thought it well to put on record the results of a few of our experiments on the Budde effect with reference to bromine.

As we wished to get comparative results, the apparatus was as follows: The vessels containing the chlorine and bromine were glass bulbs of 500 cc. capacity, provided with gas inlet and outlet tubes, each bearing a stop-cock. These were immersed in a glass vessel of water in such a way that a layer of water, 62 mm. thick, separated them from the surrounding air. The gases were passed into the respective bulbs (the temperature being such as to gasify the bromine). Each bulb was then connected with a manometer containing, in some experiments saturated sodium chloride solution, in other cases concentrated sulphuric acid.

In these experiments the apparatus was set up in a partially darkened room. The source of light was a photographic flash-light cartridge[1] exploded at a distance of 30 cm. from the outside of the water jacket.

A mean of the results of two experiments (which did not vary greatly from each other) gives the expansion of the chlorine, as indicated on the manometer scale, three divisions; the expansion of the bromine, fifty-four divisions.

The recovery of the original volume was not immediate, but extended through a period of three seconds on an average. As these experiments were of a preliminary nature, the results are not given as exact, but only approximate. The gases were not perfectly dry nor pure. Similar experiments with hydrogen, oxygen, and air gave an almost imperceptible momentary indication of disturbed volume conditions.

In other experiments ordinary florence flasks were used in the same way, and Beckmann thermometers were inserted in the gases. The rise in temperature was by no means such as to account for the changed volumes, especially in the case of bromine. The temperature, change of air, chlorine, and bromine did not differ very materially from one another.

Mellor's conclusion with regard to chlorine is:[2] "There is

[1] Eastman's Flash Cartridge, No. 2.

[2] J. Chem. Soc. (London), Trans., 81, 129 (1902).

no experimental evidence to show that chlorine gas under the influence of light undergoes any change capable of appreciably affecting the chemical activity of that element towards hydrogen." Presumably, then, there is no evidence in favor of the dissociation of chlorine molecules into ions in the sunlight. The results with bromine indicate the same general fact. Chlorine shows so much greater increased activity in sunlight than does bromine, that it should be supposed, that if the increase in volume—the Budde Effect—were caused by ionization, then this phenomenon would be far more noticeable in the case of chlorine than of bromine. This is not the case.

Whether his second conclusion[1] that the Budde Effect is entirely caused by "part of the energy absorbed by moist chlorine from sunlight being dissipated as heat" is true or not, remains to be seen. If this were the case, then the temperature rise should be much greater in the case of bromine than of chlorine, and this is not in accord with our experiments.

TULANE UNIV. OF LOUISIANA,
NEW ORLEANS, LA.,
Nov. 1, 1902.

REPORT.

Recent Advances in Our Knowledge of the Metals of the Platinum Group.

1897–1903.

It is now six years since the publication of the Bibliography of the Metals of the Platinum Group, in which the literature of these elements was brought down to the close of 1896. It is the purpose of this paper to review some of the more important advances which have been made since that time in this field.

The number of workers has not been large, chiefly due, doubtless, to the cost of the raw material, which precludes any extensive development along the line of technical chemistry, and which, except in the case of platinum itself, compels investigators to work with inconveniently small quantities of material. Yet the number of papers within our field since the beginning of 1897 is nearly two hundred.

There is little new to chronicle regarding the occurrence of

[1] *Loc. cit.*

platinum in nature. Localities and output have undergone comparatively little change. By far the greatest portion of platinum comes, as it always has, from Russia, and these workings are gradually becoming poorer, though more extensively worked. A few months ago the papers told of rich platinum placers discovered on a tributary of the Iss in the northern Uralian district, but this has not been confirmed.

Platinum in the form of sperrylite, $PtAs_2$, seems to be a constant accompaniment of the Sudbury, Ontario, nickel ores, and is concentrated in the matte to the extent of about 50 grams of platinum per ton of nickel.

The Tulameen district, in British Columbia, has been a small producer of platinum, and was in 1900 quite thoroughly studied by Prof. J. F. Kemp, of Columbia University. While the platinum there is widely disseminated, it is very sparsely distributed in the mother-rock and in a very finely divided condition, precluding the possibility of economic working by any of the methods at present in use. Prof. Kemp considers that there is little probability of extensive platinum placers being found in any but very old land areas which have been subjected to protracted denudation and concentration.

Platinum, in the form of sperrylite, and perhaps also native, has been reported from some of the Colorado mines, and also from Alaska. Unfortunately, gold miners have generally regarded platinum, as far as it has been noticed in their washings, as a nuisance, so that it is probable that large quantities of the metal have been overlooked and thrown away in gold placers.

Prof. Kemp has made a notable contribution to the literature of the occurrence of platinum in his "Geological Relations and Distribution of Platinum and Associated Metals," published in 1902 as Bulletin 193 of the United States Geological Survey. In this work Prof. Kemp has reviewed all the occurrences of platinum, treated those of the Tulameen district and of the Urals very fully, and discussed the geology of platinum deposits more completely than had previously been done. He inclines to the opinion that platinum has been deposited from fusion, contrary to the views of Meunier, who holds that the platinum is a later deposition. From a study of sections of platinum and gold nuggets, Liversidge[1] also concludes that these metals have been precipitated from aqueous solution.

It may not be out of place to state that I have, through the courtesy of Baker & Company, in my possession a specimen

[1] Proc. Chem. Soc. (London), 174, 22 (1897).

of platinum sand which is well authenticated as having come from the southern part of the Appalachian system, but from what particular locality we have never been able to ascertain.

In connection with the working of platinum, as well as gold and silver deposits, a patent has been issued[1] in Germany to Frasch, who proposes to pump a solvent such as chlorine or bromine water, or potassium cyanide, directly into the natural alluvial deposits, thereby aiming to recover the fine particles which are lost in the tailings of ordinary washing.

During the period under our consideration no new element has been reported in the platinum group, and Mallet[2] has shown that the last proposed metal, davyum, has no claim to independent existence. Large quantities of platinum residues were placed by Sir George Matthey at Dr. Mallet's disposal, and using Kern's own methods, no indication of a new metal was found. In all probability Kern's davyum was merely a mixture of iridium and rhodium.

A few new forms of platinum apparatus have been devised. Stehman[3] has improved the Shimer crucible by using brass screws and asbestos packing instead of rubber for connections, avoiding the danger of organic matter falling into the carbon.

Soltsien[4] uses a narrow bent tube of platinum, after the manner of open tubes in blow-pipe analysis, for incineration in ash determinations.

Friedrichs[5] makes a very practical handle for a platinum spatula by fastening the end into a small porcelain tube by means of fused glass.

Probably most of us have suffered by the breaking off of the platinum eudiometer wires close to the glass. Palmaer[6] protects the wire by enclosing it in a small glass tube, fused on to the apparatus, and bent upward. A drop or two of mercury in the tube serves to make convenient connections.

Cowper-Coles[7] suggests that palladium is readily deposited electrolytically from ammonium palladium chloride solutions, and gives a better reflecting surface than silver, while it is as hard as nickel.

The Heraeus electric combustion-furnace promises to become useful. The resistance is furnished by a strip of very thin platinum foil wound spirally around the glass tube. Any desired temperature up to fusion can be rapidly obtained without danger of breaking the glass. Heraeus has also

[1] D. R. P. 93178.
[2] This JOURNAL, **20**, 776 (1898).
[3] J. Am. Chem. Soc., **25**, 237 (1903).
[4] Pharm. Ztg., **42**, 293 (1897).
[5] Chem. Ztg., **22**, 917 (1898).
[6] Ber. d. chem. Ges., **32**, 2570 (1899).
[7] Chem. News, **79**, 280 (1899).

made a crucible of pure iridium in which quartz can be fused for making quartz apparatus, by means of the oxyhydrogen blowpipe.

The demand for resistant electrodes has led to improvements by Heraeus.[1] He has found that without sacrificing the durability of the electrodes, a greatly increased surface area can be obtained by using the thinnest platinum or platinum-iridium foil. This is welded to platinum wire, which is enclosed in glass tubing. The platinum wire is in turn soldered to copper conductors. For large currents an indefinite number of these individual electrodes may be combined.

The ideal material for electrodes is considered by Foerster[2] to be a 10 per cent alloy of platinum with iridium. This can be used as thin as 0.0075 mm. and is available in salt solutions, with or without diaphragm. According to Denso[3] such electrodes can be used in the presence of free acid and at any temperature. There is at first a slight loss owing to impurities, but this is only temporary. Bran[4] finds there is less loss with high current density than with low. The proportion of iridium in the alloy within limits of a few per cent has no effect, but with as much as 25 per cent the durability of the electrode is increased.

By the action of the alternating current platinum electrodes are slowly carried into solution.[5] Ruer[6] considers that this is owing to the formation of an insoluble peroxide, which is reduced by the reversed current to a lower oxide, which enters the solution. In the case of such electrolytes as ammonia, potassium cyanide, etc., complex platinum salts are formed. Low results in the electrolytic determination of mercury are attributed by Glaser[7] to the fact that the platinum cathode is soluble in potassium cyanide. Under similar circumstances gold and silver are not soluble.

In 1900 an investigation was made by Hall[8] as to the loss of weight experienced by platinum on subjection to high temperatures. He attributes the loss to the formation of a volatile oxide. This has been further studied by Holborn[9] in conjunction with Henning and Austin, and extended to other metals and alloys of the group, and to other gases than air and oxygen. In these investigations the wire or foil was

[1] D. R. P. 132588.
[2] Ztschr. f. Elektrochem., **8**, 143 (1902).
[3] *Ibid.*, **8**, 147 (1902).
[4] *Ibid.*, **8**, 197 (1902).
[5] Margules: Wied. Ann., **66**, 540, 629 (1898).
[6] Ztschr. f. Elektrochem., **9**, 235 (1903).
[7] *Ibid.*, **9**, 11 (1903).
[8] J. Am. Chem. Soc., **22**, 494 (1900).
[9] Sitzber. Akad. Wiss., Berlin, 1902, 936; 1903, 245.

electrically heated. In all cases more or less loss was sustained, the metals generally (except in the case of the iridium-rhodium alloy) became more flexible, and showe d a crystalline structure. Except in the case of iridium alloys, the loss was very small; here, however, there was a decided loss, which diminished as more iridium had been removed from the surface. It is suggested that this loss could lead to errors in thermo-elements. The loss was generally greater in oxygen than in air, and was little in nitrogen. Where oxidizing atmospheres are present, the loss must be attributed to chemical action, but in hydrogen it is probably simply a sublimation of the metal. In this connection it is interesting to note that when ruthenium is heated to 1000° in oxygen it slowly volatilizes as RuO_4, being deposited as a lower oxide in the cooler portion of the tube, although RuO_4 itself is decomposed with explosive violence at about 100°.

In studying the composition of platinum which has become brittle by use, Hartley[1] shows by the use of the spectroscope the absence of all injurious elements but carbon and phosphorus, though it is difficult to prove the absence of iron from the platinum, owing to the closeness of their characteristic lines. Rosenhain,[2] however, attributes the brittleness of platinum to a recrystallization, at temperatures slightly below its fusion-point, similar to that experienced by other metals. White-hot platinum is easily shattered by a blow. The crystalline appearance of platinum which has been highly heated is not superficial, but extends into the mass. According to Heraeus,[3] the damage to platinum crucibles in phosphate analyses is due to the fact that magnesium phosphate is readily reduced by ammonia below 900° and by carbon below 950°.

The first mention I have been able to find of the use of metallic osmium to take the place of carbon in the filament of the incandescent electric light is in Merck's Jahresbericht for 1898 (page 25). Platinum early proved too fusible; Poland tried iridium in 1890. Osmium is practically infusible by any ordinary current, but owing to the ease with which it is oxidized it must be used in a vacuum. It gives a whiter light than carbon and is more economical; since it can be run with a 25-volt current, it is advantageous for use with a storage battery.[4] The greatest and almost insuperable obstacle to its use is its cost. It should, however, be noted that osmium is the only constituent of osmiridium which has no

[1] Proc. Chem. Soc. (London), **18**, 30 (1902); Phil. Mag. [6], **4**, 84 (1902).
[2] Proc. Roy. Soc. (London), **70**, 252 (1902).
[3] Ztschr. angew. Chem., **15**, 917 (1902).
[4] Scholz: Jour. f. Gasbeleuchtung, **44**, 101 (1901).

practical use, if we except the insignificant amount of osmium tetroxide used in microscopy; and osmium composes nearly one-half of osmiridium. Various devices have been patented[1] for preparing osmium filaments, and also for preparing complex filaments of osmium alloys, of carbon impregnated with osmium, or of rare earths mingled with osmium. An osmium-platinum alloy may be heated till the platinum volatilizes; platinum wire or a carbon filament may be heated in an atmosphere of osmium tetroxide till sufficient osmium is deposited; the rare earths may be made into a paste with osmium sponge or some osmium compound, and then heated; in any case, when the osmium filament is heated to a high temperature by the current in a vacuum or in an indifferent gas it becomes a coherent metal. It is said that ruthenium gives much the same results as osmium, and can be similarly made into filaments, but its excessive rarity would render its use impracticable; indeed, it hardly seems possible at present that the osmium light should come into any general use.

No subject connected with the platinum metals has recently attracted more attention than the work of Bredig and his followers on colloidal platinum as an inorganic ferment. In 1898 Bredig[2] published an account of a very finely divided form of platinum prepared by passing a current of 6 to 10 amperes at 30 to 40 volts between platinum electrodes immersed in water. An apparent solution was obtained of a dark wine color, which did not clear up in weeks and which was very active in promoting those so-called catalytic actions which had long been known to be brought about by finely divided platinum in the form of sponge or platinum black. It was soon found that this solution, now known as colloidal platinum, possesses many of the properties of an organic ferment, and, like the latter, is so affected by the presence of certain salts and other substances that it is no strained application of the term to speak of its being poisoned.[3] This action was tested by adding the "poison" to the colloidal platinum, then adding hydrogen peroxide, and titrating the undecomposed peroxide with potassium permanganate. In the early experiments it was found that prussic acid was an active poison to the platinum, as were iodine, mercuric chloride, hydrogen sulphide, and some other compounds. Carbon monoxide, phosphorus, and phosphine were very poisonous, but the platinum soon recovered from their effect. Arsenic, hydrochloric acid, oxalic acid, and ammonium chloride were mod-

[1] D. R. P. 132428, 138135, 140468; **Abstracts in Chem. Centrbl.**, 1902, II: 83; 1903, I 209, 903.

[2] Ztschr. f. Elektrochem., **4**, 514 (1898).

[3] Bredig and Ikeda: Ztschr. phys. Chem., **37**, 1 (1901).

erately poisonous, while, so far from being injurious, formic acid, dilute nitric acid, and hydrazine might be said to have a healthy action. Alcohol, ether, and chloroform were inert. There is thus a strong similarity as regards the action of poisons upon this inorganic ferment and upon organic ferments, but by no means an identity. Raudnitz[1] considered the action due to the influence of the poison upon the catalyzed substance, pointing out that while the enzyme of milk has little effect upon hydrogen peroxide in the presence of prussic acid, the action is restored if the prussic acid be driven out by a current of air. Bredig,[2] however, holds that the poisoning is due to the action of the poison upon the catalyzer (catalyzing substance), pointing out that the analogy between organic and inorganic ferments must not be pushed too far. Sodium thiosulphate, for example, is a strong poison to the latter, but is not a poison to blood and enzyme catalysis. This work promises to throw much light upon the action of organic ferments. The action of colloidal platinum on mixtures of oxygen and hydrogen has been studied by Ernst,[3] and upon the persulphates by Price.[4] Gutbier[5] obtained a very sensitive platinum by the reduction of dilute chloroplatinic acid with hydrazine hydroxide.

Somewhat along this line are the studies of Höber[6] on the action of poisons on the oxyhydrogen cell, the electrodes being platinum foil saturated at one pole with hydrogen and at the other with oxygen. Potassium cyanide and hydroxylamine poison only the oxygen pole, while ammonium sulphide and carbon bisulphide poison both poles. Corrosive sublimate poisons the platinum oxygen very slightly, but the platinum hydrogen strongly. The action is attributed by Höber to the formation of a complex platinum salt.

The successful solution of the problem of sulphuric acid manufacture by the contact process should be mentioned here, though most of the experimental work belongs to the earlier period. An active contact substance is prepared by Majert[7] by impregnating asbestos or some similar mass with a solution of platinum chloride in alcohol or other organic solvent, and burning off the solvent. A very active platinized asbestos may be thus obtained containing not over 2 per cent of platinum. A patent[8] has also been taken out for regenerating

[1] Bredig and Ikeda: Ztschr. phys. Chem., **37**, 551 (1901).
[2] *Ibid.*, **38**, 122 (1901).
[3] *Ibid.*, **37**, 448 (1901).
[4] Ber. d. chem. Ges., **35**, 291 (1902).
[5] Ztschr. anorg. Chem., **32**, 347 (1902).
[6] Pflüger's Arch., **82**, 631 (1900).
[7] D. R. P. 134928.
[8] D. R. P. 135887.

a contact substance which has been poisoned by arsenic, by driving steam through the contact mass with the chamber gases.

The relation of platinum and palladium to gases continues to attract attention, as it has since the discovery of platinum sponge by Doebereiner eighty years ago, and the work of Graham on palladium in 1868. Randall,[1] using special precautions, finds that hydrogen passes slowly through white-hot platinum, but that toward oxygen, hydrogen, and methane the metal is perfectly impervious. Dewar[2] failed to find a critical temperature for palladium-hydrogen, the gas still being absorbed by the metal at 500° under a pressure of 120 atmospheres. The heat of combination at high temperatures is greater than at low. The experiments of Mond, Ramsay, and Shields[3] have been continued and they conclude that the compound Pd_2H does not exist, though possibly Pd_4H_3 does. Zelinsky[4] finds zinc coated with palladium-hydrogen to be a good reducing agent for alkyl bromides and iodides, hydrocarbons being formed.

A little work has been done upon the alloys of platinum. Brunk[5] finds platinum slowly dissolved by aluminium and on treatment of the regulus with dilute hydrochloric acid, crystals having the apparent composition of Pt_3Al_{10} were obtained. From these the aluminium was almost completely dissolved by more concentrated acid. Hodgkinson, Waring, and Desborough[6] obtained, by heating in a vacuum, $PdCd_2$, but the alloys with zinc and with magnesium were of more doubtful composition. No definite compounds could be obtained with these metals and palladium.

The platinum-silver alloys have always interested assayers. That silver can be dissolved out completely by concentrated sulphuric acid is confirmed by Richards.[7] The rather surprising statement was presented by Spiller[8] to the London Chemical Society that from platinum-silver alloys containing from 0.25 per cent to 12 per cent platinum, the silver could be almost completely dissolved out with nitric acid of sp. gr. 1.2 to 1.42, hardly more than a trace of platinum going into solution. This was contrary to previous experience, and more recent unpublished experiments by Lodge, and in my own laboratory, show that while the weaker the acid and the

[1] This JOURNAL, **19**, 682 (1897).
[2] Proc. Chem. Soc. (London), **183**, 192 (1897).
[3] Proc. Roy. Soc. (London), **62**, 290 (1897).
[4] Ber. d. chem. Ges., **31**, 3203 (1898).
[5] *Ibid.*, **34**, 2733 (1901).
[6] Chem. News, **80**, 185 (1899).
[7] The Analyst, **27**, 265 (1902).
[8] Proc. Chem. Soc. (London), **180**, 118 (1897).

richer the alloy in platinum, the less platinum enters solution, no regularity can be established, and in no case does all the platinum remain undissolved. The explanation of these discrepancies is doubtless that suggested by Harcourt at the Chemical Society meeting, that Spiller's alloys were not complete solutions, having been formed at too low a temperature.

No simple or satisfactory method of assay for the platinum metals in conjunction with gold has been devised, though the subject has been studied by Vanino and Seemann,[1] Peterson,[2] Rössler,[3] and Mietzschke.[4]

The use of sodium peroxide promises to simplify the decomposition of iridosmium, which has always been a difficult problem. This agent has a powerful oxidizing action upon all the metals of the group, giving soluble compounds with all except platinum and rhodium. Dudley[5] has studied its action upon platinum, while Leidié and Quennessen[6] have applied the action of sodium peroxide, combined with the subsequent use of sodium nitrate, to the separation of the metals. Leidié[7] obtains pure iridium by a sodium nitrite method distinct from that of Gibbs. Jörgensen[8] purifies rhodium from iridium by the use of the chloropentaminerhodium salts. He finds the atomic weight of this purified rhodium to be the same as that heretofore determined, indicating that the previously obtained rhodium was not contaminated by iridium. Mylius and Dietz[9] have given a full description of methods of obtaining all the platinum metals in a state of purity.

For the preparation of barium platocyanide, Bergsöe[10] treats chloroplatinic acid with barium hydroxide and sulphur dioxide, and the resultant platosulphite with barium cyanide. Or the first mixture may be treated directly with sulphur dioxide after the addition of hydrocyanic acid. An output of 75 per cent is obtained and the platinum is perfectly free from iridium. It may be questioned, however, whether for the ordinary preparation of platocyanides this equals the method of dissolving platinum sulphide in a solution of alkaline cyanide.

A not uninteresting episode was the publication of a paper[11] by Sulč showing that osmium slowly lost weight when heated in the air at 212° and in oxygen at 170°, and the rejoinder by

[1] Ber. d. chem. Ges., **32**, 1968 (1899).
[2] Ztschr. anorg. Chem., **19**, 59 (1898).
[3] Chem. Ztg., **24**, 733 (1900).
[4] Berg Hütt. Ztg., **59**, 61 (1900).
[5] This JOURNAL, **28**, 59 (1902).
[6] Bull. soc. chim. [3], **25**, 9, 840 (1901); **27**, 179 (1902).
[7] J. Pharm. Chim. [6], **10**, 163 (1899).
[8] Ztschr. anorg. Chem., **34**, 82 (1903).
[9] Ber. d. chem. Ges., **31**, 3187 (1898).
[10] Ztschr. anorg. Chem., **19**, 318 (1899).
[11] *Ibid.*, **19**, 332 (1899).

Vèzes[1] that Deville and Debray long ago showed that osmium, when finely divided, slowly volatilizes as osmium tetroxide even at ordinary temperatures. The rapidity of this oxidation depends merely upon the fineness of the osmium.

Turning now to the halide compounds of platinum, Mallet[2] finds that platinum sponge precipitated by formaldehyde is, after exposure when damp to the air, somewhat soluble in rather strong hydrochloric acid. Méker[3] prepares the bromoplatinates by heating the metal with ammonium sulphate and a bromide to 350°. Very important is a new method discovered by Vèzes[4] of preparing potassium chloroplatinite, which comes as a great relief to those who have been used to preparing the salt, for photographic and other purposes, by reducing the chloroplatinate with cuprous chloride, sulphur dioxide, or even by heat. In his work on the platoxalates, Vèzes found that by boiling the chloroplatinate suspended in water with the calculated amount[5] of potassium oxalate for several hours, it is quantitatively converted into the chloroplatinite. A large portion of the salt crystallizes out on cooling, while the balance may be recovered by evaporation and precipitation with alcohol.

In 1878 Pitkin[6] prepared a supposed mixed haloplatinate by the addition of potassium bromide to chloroplatinic acid. This was shown by Herty[7] and others to be an isomorphous mixture. Miolati[8] has, however, prepared a true bromochloroplatinate by the addition of bromine to potassium chloroplatinite. Its composition is $K_2PtCl_4Br_2$. I have myself found that when hydrogen bromoruthenite is precipitated by potassium chloride, potassium bromoruthenite, K_2RuBr_5, is formed, free from chlorine.

The use of chloroplatinic acid in potash determinations has been studied by Atterberg[9] and Rohland,[10] with no suggestions of a change from the ordinary procedure. The residues from analysis are treated for the recovery of platinum with aluminium turnings by Wiley,[11] with magnesium by Atterberg,[12] and with zinc dust by Berthold.[13] Knoevenagel and Ebler[14] find

[1] Ztschr. anorg. Chem., **20**, 230 (1899).
[2] This JOURNAL, **23**, 430 (1901).
[3] Compt. rend., **125**, 1029 (1897).
[4] Bull. soc. chim. [3], **19**, 879 (1898).
[5] 100 grams K_2PtCl_4, 37 grams $K_2C_2O_4.H_2O$, suspended in 1 liter of water.
[6] J. Am. Chem. Soc., **1**, 472 (1878); **2**, 296, 408 (1879).
[7] *Ibid.*, **18**, 130 (1896).
[8] Ztschr. anorg. Chem., **14**, 237 (1897).
[9] Chem. Ztg., **22**, 522, 538 (1898).
[10] Ztschr. anorg. Chem., **15**, 412 (1897); **16**, 305 (1898).
[11] J. Am. Chem. Soc., **19**, 258 (1897).
[12] *Loc. cit.*
[13] Ztschr. angew. Chem., **14**, 621 (1901).
[14] Ber. d. chem. Ges., **35**, 3055 (1902).

that hydrazine precipitates platinum completely in caustic soda or acetic acid solutions, but incompletely in the presence of ammonia or a mineral acid. Hydrogen peroxide does not precipitate it at all, nor does hydroxylamine, except a partial precipitation in ammoniacal solutions.

In their remarkable work upon the basic properties of nitrogen, Baeyer and Villiger[1] use chloroplatinic acid as a weak acid to form salts with oxygen bases, and suggest that cyanoplatinic acid, $H_2Pt(CN)_4$, can probably be similarly used. The compound formed when hydrochloric acid acts upon an alcoholic solution of potassium cyanoplatinite seems to be a salt, $2C_2H_5OH,H_2Pt(CN)_4$, in which alcohol plays the part of a base.

By far the most interesting chapter of the work upon the platinum halides is that which has been most largely developed by Miolati on the different chloroplatinic acids, and the discovery of which we owe almost exclusively to modern physico-chemical methods. In 1870 S. A. Norton[2] described a new chloride of platinum, $PtCl_4.5H_2O$. In 1898 Sonstadt[3] studied the action of a large amount of water upon chloroplatinic acid. He found that in hot water decomposition takes place with the formation of a chloride of platinum, PtCl. This change he later[4] found to take place in cold water under the influence of light. The same year Kohlrausch[5] noted that the solution of Norton's tetrachloride acted as an electrolyte, and suggested that there seemed to be formed an acid, H_2PtCl_4O. The next year this acid was carefully investigated by Hittorf and Salkowski[6] and its existence confirmed by the preparation and analysis of its silver salt. In 1900 Kohlrausch[7] studied further the hydrolysis of both chloroplatinic acid and Norton's tetrachloride, and Dittenberger and Dietz[8] considered that the tetrachloroplatinic acid, H_2PtCl_4O, was decomposed into the ordinary hexachloroplatinic acid and a compound $PtCl_2O$.

The subject was now taken up by Miolati, partly in conjunction with Bellucci. In his first article[9] he gives a resumé of the matter, showing that the true tetrachloroplatinic acid has the formula $H_2PtCl_4(OH)_2$, describes the silver, zinc, cadmium, thallium, and lead salts, and then goes on to show the great probability that numerous other derivatives and de-

[1] Ber. d. chem. Ges., **34**, 2679 (1901); **35**, 1201 (1902).
[2] J. prakt. Chem. [2], **3**, 469 (1870); **5**, 365 (1872).
[3] Proc. Chem. Soc. (London), **188**, 25 (1898).
[4] *Ibid.*, **198**, 179 (1898).
[5] Ann. phys. Chem. [2], **63**, 423 (1898).
[6] Ztschr. phys. Chem., **29**, 546 (1899).
[7] *Ibid.*, **33**, 257 (1900).
[8] Ann. phys. Chem. [2], **68**, 853 (1899).
[9] Miolati: Ztschr. anorg. Chem., **22**, 445 (1900).

composition-products of the hexachloroplatinic acid are in reality to be considered as various members of a series of acids, all derived from the ordinary chloroplatinic acid, H_2PtCl_6, by the replacement of one or more atoms of chlorine by the hydroxyl group. These he calls the mono-, di-, tri-, etc., chloroplatinic acids. Jörgensen's $PtCl_3O.H_2O$ is an anhydride of dichloroplatinic acid; the well-known precipitate formed by the action of lime-water on chloroplatinic acid in the sunlight is the calcium salt of monochloroplatinic acid. In the hands of these two chemists the work rapidly developed until now salts of each member of the series have been prepared with the exception of the trichloroplatinic acid; salts of trichloroplatinous acid, H_2PtCl_3OH, have, however, been formed. Several of the other haloplatinic acids have also been made.

Pentachloroplatinates[1] are derived by the action of fused caustic potash upon hexachloroplatinic acid; monochloroplatinates[2] by lime-water, as above, dichloroplatinates[3] by the action of ammonia on tetrachloroplatinic acid; trichloroplatinites[4] by the evaporation of tetrachloroplatinous acid in a vacuum; tetrabromoplatinates[5] and tetraiodoplatinates[6] similarly to the chlorine salts. Efforts have been made by Miolati and Bellucci[7] to prepare similar salts where the halides are replaced by other groups, but they have thus far failed. Halocyanates such as $Ag_2Pt(CN)_4Cl_2$, and halonitrites, as $K_2Pt(NO_2)_4Br_2$, have, however, been obtained. These are similar to the complex platinum salts of Vèzes, shortly to be considered.

To this may be added the work of de Coninck[8] on another form of decomposition of platinum chloride, by filtration through animal charcoal, or by the action of such salts as magnesium sulphate in sunlight.

During the past six years Prof. Vèzes, of the University of Bordeaux, has given much time to the investigation of the complex platinum acids. If potassium platonitrite (to use the old nomenclature), $K_2Pt(NO_2)_4$, is treated with oxalic acid, the platooxalate is obtained. This reaction proceeds in two stages, and the intermediate product, the platooxalonitrite, $(K_2PtOx(NO_2)_2.H_2O)$, is easily prepared.[9] This reaction may be used practically to separate platinum from all the

[1] Miolati and Bellucci: Ztschr. anorg. Chem., **24**, 209 (1901).
[2] Bellucci: Atti. R. Accad. Lincei, Roma [5], **11**, II, 241, 271 (1902).
[3] Miolati and Pendini: Ztschr. anorg. Chem., **33**, 251 (1903).
[4] Miolati and Pendini: *Ibid.*, **33**, 264 (1903).
[5] Miolati and Bellucci: *Ibid.*, **24**, 222 (1901).
[6] Bellucci: Atti R. Accad. Lincei, Roma [5], **11**, I, 8 (1902).
[7] Gazzetta, **30**, II. 588 (1901).
[8] Compt. rend., **130**, 1551 (1900); Bull. Acad. Roy. Belg., 1902, 730.
[9] *Ibid.*, **125**, 525 (1897); Bull. soc. chim. [3], **21**, 481 (1899).

other members of the group. The salts of the alkalies and alkaline earths were obtained, as well as a double potassium barium salt.[1] The salts of the heavy metals decompose at once into the oxalates, and the free acid itself is too unstable to be obtained by evaporation.[2] The reaction between the platonitrites and potassium oxalate on the one hand, and the platooxalate and potassium nitrite upon the other, is a reversible reaction. The same is true where the platinum-chloronitrite ($K_2PtCl_2(NO_2)_2$) is substituted for the simple platonitrite.[3] The same is again true of the reaction in passing from the chloroplatinite to the platooxalate by the addition of potassium oxalate.[4] I have found a similar reaction between the chlororuthenite and oxalic acid, which has thus far negatived my efforts to separate the ruthenooxalate. It was in connection with his work upon these oxalates that Vèzes recognized that the first action of potassium oxalate upon chloroplatinates is that of reduction to the chloroplatinites, which has already been noted in connection with the preparation of the latter salt.

In 1893 Vèzes found that if a solution of a platonitrite be acidified and warmed, a peculiar salt is formed which is copper-red in color, but gives an almost colorless solution. This reminds one of the so-called platoplaticyanides of Knop and Schnedermann, which are formed by the addition of a trace of an oxidizing material, such as chlorine, to a concentrated solution of platocyanide. The constitution of these cyanides was cleared up by Hadow, who showed that they are a combination of 5 molecules of a platocyanide with 1 molecule of a platicyanide. Werner anticipated that Vèzes' red platinonitrite would prove to have a similar composition, but its analysis shows it to have the formula $K_2H_4Pt_3O(NO_2)_6$, which seems to indicate a reduction rather than an oxidation.[5] Meantime Miolati[6] has obtained a similar or identical red salt by the dry heating of addition-products, $K_2Pt(NO_2)_4,N_2O_4$ and $K_2Pt(NO_2)_4,HCl$, of the platinonitrite, and Vèzes himself[7] has obtained similar salts in the attempt to form platonitrites of copper.

In studying the platooxalates, Werner[8] has found two classes of salts, one yellow and the other dark-red, and suggests the possibility of stereoisomerism.

[1] Bull. soc. chim. [3], **27**, 157 (1901).
[2] *Ibid.* [3], **29**, 83 (1903).
[3] *Ibid.* [3], **21**, 143 (1899).
[4] Ann. chim. Phys. [7], **15**, 444 (1898).
[5] Vèzes: Ztschr. anorg. Chem., **15**, 278 (1897).
[6] Atti R. Accad. Lincei, Roma [5], **5**, II, 355 (1896).
[7] Bull. soc. chim. [3], **27**, 930 (1902).
[8] Ztschr. anorg. Chem., **21**, 377 (1899).

Some little work has been done during the last few years upon the platinum bases, but little has been added to our knowledge of the constitution of these interesting compounds. Two papers have appeared on the subject from Jörgensen,[1] which reveal the fact that he still remains antagonistic to the views of Werner. He has changed his opinion in one particular, in that he now considers Peyrone's base to possess the symmetrical formula, $Pt\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}$, while Reiset's second chloride is the symmetrical form, $Pt\begin{matrix}NH_3.NH_3Cl\\Cl\end{matrix}$. He also draws interesting analogies between these bases and the ethylene bases (acechlorplatin, etc.) of Zeise. Prandtl and Hofmann[2] and Bülmann[3] have also worked along this line, the former making the ethylene base by the action of chloroform on chloroplatinic acid, and the latter forming similar compounds with allyl alcohol. Werner[4] has prepared a series of acetylacetone compounds; while Uhlenhuth[5] obtains with hydroxylamine two isomeric bases of the formula

$$Pt(NH_3OH)_2Cl_2$$

as well as a tetrahydroxylamine base. Cossa,[6] who also adheres to the Blomstrand theory of the constitution of the platinum bases, presents a paper on the missing member of the amine series, that in which but a single ammonia group is present, and has prepared a number of derivatives of the chloride. While he has not succeeded in isolating the chloride itself, he has prepared the thiocyanate, $Pt(NH_3)(SCN)_2$.

The most important paper upon this subject is that of Klason,[7] who treats the bases at length, both from a theoretical and an experimental standpoint. He considers the ammonia to be present in two forms, in one of which it is united solely to the platinum atom and in the other to both platinum and the negative element or group; the former class he distinguishes by the prefix "an." This is analogous to the linking of oxygen to carbon in the carbonyl group, while the other form would resemble the oxygen in the hydroxyl group. This classification and nomenclature then becomes the following:

[1] Ztschr. anorg. Chem., **24**, 153 (1900); **28**, 253 (1900).
[2] Ber. d. chem. Ges., **33**, 2981 (1900).
[3] *Ibid.*, **33**, 2196 (1900).
[4] *Ibid.*, **34**, 2584 (1900).
[5] Ann. Chem. (Liebig), **311**, 120 (1900).
[6] Ztschr. anorg. Chem., **14**, 367 (1897).
[7] J. prakt. Chem. [2], **67**, 1 (1903).

Class I. 1. NH_3PtCl_3. Platosemianamine chloride.
2. $ClPtNH_3Cl$. Platosemiamine chloride.

Class II. 1. $(NH_3)_2PtCl_2$. Platoanamine chloride.
2. $NH_3Pt\langle^{NH_3Cl}_{Cl}$. Platosemianaminesemiamine chloride.
3. $Pt(NH_3Cl)_2$. Platoamine chloride.

Class III. 1. $(NH_3)_2Pt\langle^{NH_3Cl}_{Cl}$. Platoanaminesemidiamine chloride.
2. $NH_3Pt(NH_3Cl)_2$. Platosemianaminediamine chloride.

Class IV. $(NH_3)_2Pt(NH_3Cl)_2$. Platodiamine chloride.

How this new aspirant for favor will be received by the respective advocates of the Blomstrand and the Werner theories remains to be seen, and what is more important, how it will explain the numerous mixed compounds and isomers of the group. Klason[1] himself has already applied it successfully to mixed platophosphinamine isomers.

Among the few remaining papers on platinum which we find in this period are one by Hofmann and Rabe[2] on derivatives of platinum mercaptides; one by Müller,[3] who finds carbon monoxide has no action on the platocyanides; one by Granger,[4] who forms three definite phosphides of platinum, Pt_2P_3, Pt_2P, and PtP_2, by heating phosphorus and platinum in an atmosphere of carbon dioxide; one by Roessler,[5] who has prepared three tellurides, Pt_2Te, PtTe, and $PtTe_2$; one by Harbeck and Lunge,[6] who find that both platinum and palladium absorb carbon monoxide, probably forming compounds, and hence cannot be used in gas analysis to convert ethylene into ethane if carbon monoxide be present; and, finally, a recommendation by Valenta[7] to improve the platinum toning-bath by the addition of an equal quantity of a 1 per cent solution of metaphenylenediamine.

Turning now to the other metals of the platinum group, one cannot but deplore the small amount of work which has been done, for, though the elements are rare and expensive, it is by work upon just such rare elements that we may hope for the greatest additions to our knowledge of chemical compounds in general. This applies, of course, equally well to our lack of any considerable knowledge of such elements as

[1] J. prakt. Chem. [2], **67**, 41 (1903).
[2] Ztschr. anorg. Chem., **14**, 293 (1897).
[3] Bull. soc. chim. [3], **29**, 27 (1903).
[4] Compt. rend., **123**, 1284 (1896).
[5] Ztschr. anorg. Chem., **15**, 405 (1897).
[6] *Ibid.*, **16**, 50 (1897).
[7] Phot. Corr., 1899.

columbium, tantalum, uranium, tungsten, tellurium, molybdenum, vanadium, titanium, indium, and perhaps some others. I can make no better suggestion to a young chemist than to take up one of these elements as a life study.

Beginning with palladium, we find that Vèzes[1] has extended his work on platinum oxalates to this metal, obtaining palladooxalates by similar reactions from both chloride and nitrite, and Loiseleur[2] has prepared the free palladooxalic acid, $H_2PdOx_2.6H_2O$. Intermediate compounds, as the oxalonitrites, were not found by them, but Rosenheim and Itzig[3] have, however, obtained not only oxalonitrites but also iodonitrites, and a peculiar chlorosulphite of the formula

$$(NH_4)_3PdCl_3SO_3.H_2O.$$

This seems to be a salt of mixed chloropalladous and palladosulphurous acid, $H_2PdCl_3\diagup\!\!\!\diagup SO_3H$, an interesting combination.

The distinct yellow orthorhombic crystals of potassium palladonitrite are used by Pozzi and Couquet[4] for the purpose of detecting palladium in microchemical reactions.

Rosenheim and Maas[5] have prepared several pyridine palladi bases by the action of the halogens on the pallado base, while Kurnakow[6] has studied the palladoethylenediamine bases, as well as those of thiocarbamide.

The aniline, pyridine, quinoline, and piperidine bases have been prepared by Hardin,[7] and the first-mentioned was used for the atomic weight determination of palladium. The results obtained give the figure 107.014, which is slightly higher than that of most previous determinations. Fink[8] has examined the action of carbon monoxide on palladous chloride and finds three compounds, $PdCl_2,CO$, $2PdCl_2,3CO$, and $PdCl_2,2CO$, resembling the corresponding platinum compounds. In conclusion, it may be noted that palladous chloride has been recommended by Cohen[9] as a remedy for tuberculosis.

In the study of rhodium, Jörgensen[10] has continued his papers upon the constitution of the cobalt, chromium, and

[1] Bull. soc. chim. [3], **21**, 172 (1899).
[2] Compt. rend., **131**, 262 (1900).
[3] Ztschr. anorg. Chem., **23**, 28 (1900).
[4] Compt. rend., **130**, 1073 (1900).
[5] Ztschr. anorg. Chem., **18**, 331 (1898).
[6] *Ibid.*, **22**, 384 (1900).
[7] J. Am. Chem. Soc., **21**, 943 (1899).
[8] Compt. rend., **126**, 646 (1898).
[9] Pharm. Ztg., **46**, 131 (1901).
[10] Ztschr. anorg. Chem., **14**, 404 (1897); **16**, 184 (1898); **19**, 109 (1898).

rhodium bases, but his attention has been largely devoted to combatting the views of Werner. In one of the latest papers before his death, Joly,[1] to whom we owe so much of our knowledge of the chemistry of the platinum metals, in conjunction with Leidié, described a number of salts formed by heating the double rhodium nitrites, in which the rhodium oxide, RhO_2, acts as an acid-forming oxide, thus bringing the metal in this respect into line with iridium and the other metals of the group. The salts formed were $K_2O,6RhO_2.6–8H_2O$, $Na_2O,8RhO_2.11–12H_2O$, and $BaO,12RhO_2.15–16H_2O$. Leidié[2] has prepared the potassium rhodicyanide, $K_3Rh(CN)_6$, isomorphous with the corresponding ferri-, cobalti-, mangani-, and chromicyanides. He[3] has also prepared the anhydrous rhodium trichloride, $RhCl_3$, by heating the corresponding double salts at 440° in a current of dry hydrochloric acid. By heating ammonium chloroiridate similarly in dry chlorine, he gets the iridium trichloride, $IrCl_3$.

Along this line the most noteworthy piece of work is the preparation of the series of rhodium alums by Piccini and Marino,[4] and of the rubidium iridium alum by Marino.[5] Heretofore, indium has been the only element with an atomic weight greater than 59 from which alums have been formed, but the introduction of iridium to the list shows that the formation of alum is not, as has been supposed by many, a property exclusively of elements of low atomic weight. This opens a large field in which we may expect further results from Piccini, who has already so broadened our knowledge of this interesting class of double salts.

The only other work to chronicle under iridium is a further examination of the iridonitrites by Leidié,[6] the preparation of a series of iridochloronitrites, of formula $K_3IrCl_4(NO_2)_2$, by Miolati and Gialdini,[7] and a continuation of the studies of the iridiumamine bases by Palmaer.[8]

This brings us to the two remaining, and in some respects the most interesting, metals of the group, osmium and ruthenium. Osmiamic acid has attracted the attention of chemists since the days of Fritsche and Struve, its discoverers. Joly, after his elucidation of the nitrosoruthenates, considered osmiamic acid also to be a nitroso compound, assign-

[1] Compt. rend., **127**, 103 (1898).
[2] *Ibid.*, **130**, 87 (1900).
[3] *Ibid.*, **130**, 1249 (1899).
[4] Ztschr. anorg. Chem., **27**, 62 (1901).
[5] Gazz. chim. ital., **32**, II, 513 (1903).
[6] Ann. chim. Phys. [7], **26**, 479 (1902).
[7] Gazz. chim. ital., **32**, II. (1903).
[8] Ztschr. anorg. Chem., **13**, 211 (1896).

ing it the constitutional formula of $HOOs(=O)_2-NO$, in other words, a nitrosoosmous acid. This formula and constitution was confirmed by Brizard.[1] This is, however, questioned by Werner and Dinklage,[2] who obtain on treating the osmiamates with hydrochloric acid, salts of what they call nitrilopentachlorooosmic acid, $K_2(OsNCl_5)$. They consider that osmiamic acid has the formula $HN=Os(=O)_2=O$, that is, it is the imine of osmium tetroxide, but that the salts have the tautomeric formula $RO-Os(=N)_2=O$. I cannot help feeling that this diagnosis of the case is a little doubtful, the more so as the formation of osmiamic acid from osmium tetroxide seems to be the result of reduction.

Rosenheim[3] alone, and in conjunction with Sasserath, has obtained a rather remarkable series of complex osmium sulphites and another of osmium chlorosulphites. By treatment of one of these salts with hydrochloric acid he obtains Na_2OsCl_{12}, which must be considered as sodium chloroorthoosmite, the chlorine derivative of the hypothetical orthoosmic acid, $Os(OH)_6$. This salt is almost, if not entirely, unique, and if Werner's views are true, would present a rather crowded coordinated group as the nucleus of the molecule.

The most important work on osmium is the thesis of Wintrebert,[4] which has been in part published from time to time in the French journals.[5] Much space is given to methods of analysis. In many cases the determination of the osmium was carried out by filtration through a peculiar form of Gooch tube, from which the osmium could be removed by heating in a current of air or oxygen. This permits the ready analysis of the silver salts. No worker on osmium should overlook this work. Wintrebert has prepared series of osmyl nitrites, osmyl halides, osmyl oxalates, and osmyl sulphites, of which the osmyl chloride, $K_2OsO_2Cl_4$, may be taken as a type, corresponding to the so-called oxychlororuthenites, $Cs_2RuO_2Cl_4$, previously prepared by me; a series of osmyloxy-salts, including chloride, bromide, oxalate, and nitrites, of which

[1] Bull. soc. chim. [3], **21**, 170 (1899).
[2] Ber. d. chem. Ges., **34**, 2698 (1901).
[3] Ztschr. anorg. Chem., **21**, 122 (1899); **24**, 420 (1900).
[4] L. Wintrebert: Thesis, University of Bordeaux, Paris, 1902.
[5] Compt. rend., **131**, 264 (1900); **132**, 824 (1901); Bull. soc. chim. [3], **27**, 569 (1902) (with Vèzes); Ann. chim. Phys. [7], **28**, 15 (1903).

$(NH_4)_2OsO_3Cl_2$ is an example; a series of bromosmates and iodoosmates corresponding to the chloroosmate, K_2OsCl_6; a series of nitrosochlorooosmates, bromoosmates, and iodoosmates, of which $K_2Os(NO)Cl_5$ is one, corresponding to the nitrosoruthenates; and finally an osmonitrite of the formula $K_2Os(NO_2)_5$, analogous to Joly's ruthenonitrite, $K_2Ru(NO_2)_5$. The whole thesis is a remarkable piece of work.

There have been several workers upon ruthenium in the last six years. Brizard[1] continued the work of Joly upon the nitrites, preparing several derivatives of the nitroso compounds $Ru_2H_2(NO)Cl_3$ and $Ru_2H_2(NO)Cl_5$, reduction-products of the ordinary nitrosochlororuthenate. Miolati and Tagiuri[2] consider that when chlorine acts upon a mixture of ruthenium and potassium chloride, the chlororuthenate, K_2RuCl_6, is first formed, but this breaks up into the hydrated chlororuthenate, $K_2RuCl_5.H_2O$, and this, in turn, on evaporation loses its water, becoming the ordinary chlororuthenite, K_2RuCl_5. They have also formed several sulphites and nitrososulphites. Several papers have been published by Antony and Lucchesi. They obtain ruthenium thiosulphate[3] by the action of sulphur dioxide upon ruthenic sulphate, $Ru(SO_4)_2$; by the careful solution of potassium ruthenate, (K_2RuO_4), in hydrochloric acid[4] and evaporation in a vacuum-desiccator, they obtain the long sought for potassium chlororuthenate, K_2RuCl_6; they form the ruthenic sulphate, $Ru(SO_4)_2$, by the action of sulphuric acid on barium ruthenate; a sulphite,[5] $Ru_2(SO_3)_3$, is obtained; and the two sulphides,[6] RuS_3 and RuS_2, are prepared by the action of hydrogen sulphide upon the chlororuthenate. This trisulphide has been also obtained by me, by the action of hydrogen sulphide on potassium ruthenate.

My own work upon ruthenium during the past six years has been largely devoted to the halide compounds,[7] though some work upon the ruthenocyanides,[8] partly in conjunction with H. D. Campbell, established their almost complete isomorphism with the corresponding ferrocyanides.

By the solution of potassium ruthenate, K_2RuO_4, or ruthenium tetroxide, RuO_4, in hydrochloric acid, under ordinary circumstances the chlororuthenite, K_2RuCl_5, is formed, the chlororuthenate, K_2RuCl_6, being very unstable. If, however, caesium or rubidium chloride be present, the intermediate oxychlororuthenate, $Cs_2RuO_3Cl_4$, can be obtained, a salt de-

[1] Compt. rend., **129**, 472 (1899); Ann. chim. Phys. [7], **21**, 311 (1900).
[2] Gazz. chim. ital., **30**, II, 511 (1901).
[3] *Ibid.*, **28**, II, 139 (1898).
[4] *Ibid.*, **29**, I, 312 (1899); **29**, II, 82 (1899).
[5] *Ibid.*, **30**, II, 71 (1900).
[6] *Ibid.*, **30**, II, 539 (1901).
[7] J. Am. Chem. Soc., **23**, 775 (1901).
[8] *Ibid.*, **18**, 981 (1896); **20**, 29 (1898).

composing instantly in water, and corresponding to Wintrebert's osmyl chloride. Hydrochloric acid changes this into the chlororuthenate or chlororuthenite, probably according to the temperature used. Under some conditions the chlororuthenate can be obtained directly by the action of ruthenium tetroxide on a solution of caesium chloride in hydrochloric acid, and this was my first preparation of the salt.

When a chlororuthenite is boiled with dilute alcoholic hydrochloric acid it is converted into a much more stable salt containing 1 molecule of water, $K_2Ru(H_2O)Cl_5$. This water is removed only at 180° and leaves a chlororuthenite, K_2RuCl_5, entirely different in properties from the ordinary chlororuthenite, with which it is isomeric. This salt, which, for want of a better name, I have denominated "aquo"-chlororuthenite, is itself isomeric with Miolati's hydrated chlororuthenite, but bears no resemblance to it in properties. When chlorine is added to the "aquo" salt, the chlororuthenate, K_2RuCl_6, is formed, corresponding in properties to the caesium and rubidium chlororuthenates previously prepared by me. It is quite distinct in its properties from the chlororuthenate described by Antony, so that there appears here again to be a case of isomerism. More recently I have prepared a number of bromine derivatives, which resemble closely the chlorides in their property of forming "aquo" salts, which in turn seem capable of uniting with bromine to form bromoruthenates. What the nature of the "aquo" salts may be is at present wholly a matter of conjecture. They seem to be much more ready to undergo reactions than the ordinary salt, as is shown by their union with chlorine, and by the fact that they act much more readily with oxalic acid than the ordinary salt to form oxalates.

The most striking point to me in this survey of the recent additions to our knowledge of the metals of the platinum group is not what has been attained, but rather the great field before us, upon which we have as yet hardly entered.

JAS. LEWIS HOWE.

REVIEWS.

DIE HERSTELLUNG DER AKKUMULATOREN. Von F. GRÜNWALD. Dritte Auflage. Verlag von W. Knapp. Halle a. S.

The author presents a "guide" to the construction, maintenance, and operation of the storage cell. While intended primarily for electrical engineers, it contains much more of the chemistry and electrolysis of the accumulator than is

usual in a book of this class. The treatment is restricted to the lead peroxide-sulphuric acid cell, which is shown to be a peculiar case of the primary cell from a consideration of the potential series of the metals in sulphuric acid. There is a general treatment of the electrochemistry of the primary cell, which is shown to be reversible in the particular case of the lead-lead peroxide cell. The electrolysis of sulphuric acid is discussed with the influence thereon of change of resistance due to changes of temperature and concentration, current density, migration of the ions, and polarization or counter currents, due to a change in nature of the electrodes. There is a chapter and table giving the electrolysis of the various sulphuric acids, and various compounds of lead with acids of this class. The value of porous electrodes is treated, and the physical and chemical properties of the raw materials, lead, the lead compounds, and sulphuric acid are given at some length.

The composition and method of mixing and applying the paste to the electrodes is given in detail.

The description of the various types of cell is limited to those of German manufacture.

There are complete instructions with examples for the installation and operation of batteries for various capacities and conditions of service.

The size of the volume is convenient, the illustrations are good, there are several convenient tables, but there is no index. J. B. W.

RADIUM AND OTHER RADIO-ACTIVE SUBSTANCES; POLONIUM AND THORIUM, WITH A CONSIDERATION OF PHOSPHORESCENT AND FLUORESCENT SUBSTANCES, THE PROPERTIES AND APPLICATIONS OF SELENIUM AND THE TREATMENT OF DISEASE BY THE ULTRA-VIOLET LIGHT. By WILLIAM J. HAMMER, Consulting Electrical Engineer. New York: D. Van Nostrand Company. 1903. 8vo. pp. viii + 72.

This is a lecture delivered at a meeting of the American Institute of Electrical Engineers and the American Electrochemical Society, in New York, April 17, 1903. The lecture was profusely illustrated and an attempt is made to give the reader of the book an idea of the experiments performed and specimens exhibited. To quote from an introductory note: "The author of this paper has endeavored to exemplify certain fundamental principles connected with the phenomena upon (*sic*) which he has treated; and in considering these subjects, all of which may be said to be on the borderland of science, to bring out by means of experiments, lantern slides, and illustrations which accompany the paper the practical and commercial side." "The practical and commercial side" of

radium and polonium is good. This recalls the remark that has recently gone the rounds of the newspapers: "It is utter foolishness to pay $1,500,000 for 8 oz. of radium when you can get the same quantity of polonium for $1,000,000, which will answer just as well for almost all domestic purposes."

Although Mr. Hammer's book is badly put together and is inexcusably bad from the literary as well as the purely scientific point of view, it is interesting and valuable. The author has been in communication with many of the investigators of whose work he attempts to give an account, and this gives freshness to the presentation though it also gives the impression of a certain amount of egotism on the part of Mr. Hammer. On page 19 he says: "The tiny brown bulb which I hold in my hand is the duplicate of the one which Prof. Curie showed me at his laboratory last Fall, which contained the only sample of chemically pure radium in the world." On the preceding page occurs this passage: "In a letter recently received by the author from Prof. Curie bearing upon the question of heat given off by radium Prof. Curie writes as follows: "Since the time I had the honor to see you at our school of physics and chemistry I have continued to investigate into the radio-activity induced by radium and the way that radio-activity is disappearing in the course of time."

"In a study of another kind (in collaboration with M. Laborde) I found that the radium is setting off heat continually and in a very large amount, each gram of the radium is setting off in each hour 100 small calories, or in other words, it is setting off heat enough to melt in each hour its own weight in ice."

"Where is the source of energy? Both M. Curie and myself are not able to go beyond some hypothesis."

On page 20 there is this sentence: "Prof. Curie took this ring which I have on my hand, which contains a small diamond, into his dark room and holding near it a small pill box containing about a gram of radium, caused the stone to phosphoresce most beautifully."

Selenium is taken up on account of the change in its electrical resistance that is brought about by exposing it to light. Bell's radiophone, Duddell's talking arcs, and Ruhmer's wireless telephone are described under selenium. Finally, the work of Finsen on the treatment of disease by ultra-violet rays is discussed. Here, again, the author's self-consciousness shows itself as in the passage: "The little cut of Prof. Finsen which heads this article is from an autograph portrait which Prof. Finsen presented to the writer." I. R.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By WILLIAM A. NOYES, Professor of Chemistry in the Rose Polytechnic Institute. New York: Henry Holt & Co. 1903. pp. 524.

This book is intended for beginners. The author advises the student "to *read* all of the book as well as thoroughly to master, by careful study, some portions of it." He says: "The attentive reader will, by this means, gradually absorb many ideas by a process which is closely akin to the acquisition of a language by a child."

To quote further from the preface: "The most radical departure from the method of treatment adopted in other books treating of the same subject consists in the dropping of the division into 'fatty' and 'aromatic' compounds and in the adoption of what appears to the author a more fundamental and logical classification. This novelty of arrangement will, it is hoped, be found to be justified partly by the fact that so many connecting links are now known between the two classes of bodies that they no longer stand isolated from each other; and further it is believed that the new method of treatment brings out the important contrasts in chemical conduct for the two series fully as well as the old."

The further classification is described briefly by the author in the introduction: "The hydrocarbons are considered first, as heretofore, and all classes of them together. Then follow oxygen compounds and compounds containing halogens, nitrogen, and sulphur, and finally, three chapters upon heterocyclic compounds, alkaloids, and compounds of physiological and pathological interest."

The book is undoubtedly scholarly. The author understands his subject and has a wide knowledge of it. He is, further, extremely painstaking and accurate, and he writes clearly. His judgment in the selection of his material is worthy of praise, and the arrangement of the material is logical—severely so. In short, in the opinion of the writer, the book is a good one, but he ventures to doubt whether the severely logical method adopted by the author is the best for beginners. Chapter VII. (pages 93–113) gives a very good account of the benzene series, including a clear and fairly full discussion of the structure of the fundamental hydrocarbon of the group. Succinylo-succinic ester and dihydroxyterephthalic ester, Ladenburg's prism formula, the Kekulé formula, the Claus formula, the thermochemical results of Brühl and of Thomsen are presented, and then, referring to the formulas, the author says: "The choice among these formulæ and their interpretation must be considered at present as uncertain. The proper attitude for a beginner, at least, is to

look upon the question as still an open one, and gradually to gather in his mind evidence as to one view or another till enough has been accumulated for an independent judgment."

"So far as the practical investigation of aromatic compounds is concerned, the questions last discussed have little interest. In the study of these compounds the cyclic unions are the only ones which require consideration for almost all cases."

Chapter VIII. (pages 114–120), presents the most complex hydrocarbons, including, of course, naphthalene, anthracene, and phenanthrene. Triphenylmethane and triphenylmethyl appear here also. In regard to triphenylmethyl the student is told that "It is the only hydrocarbon known which contains an odd number of carbon atoms." Of course, the author means "hydrogen atoms" instead of "carbon atoms."

Alcohols and phenols are taken up together in Chapter X (pages 124–163). The chapter begins with a helpful and perfectly correct list of all sorts and conditions of alcohols and phenols and their structural formulas. That list will strike terror into the breasts of beginners, and other tables of the same kind will be likely to produce the same result. There are two ways of teaching a subject. One is to make it easy at first and "hard" afterward as the beginner gets strength. The other is to make it "hard" at first, in the hope that it will become easy as the student goes on. It is, in general terms, the latter method that Professor Noyes adopts. Perhaps he is right. Who is to decide? The writer of this notice confesses to a leaning, perhaps too great a leaning, to the other methods.

"Triazoacetic acid" is given on page 463, although Hantzsch and Silberrad have shown that the acid to which Curtius gave this name on the supposition that it has the formula $(CHN_3.COOH)_3$, in reality has the formula $(CHN_3.COOH)_2$. I. R.

DESCRIPTIVE CHEMISTRY. By LYMAN C. NEWELL, PH.D. (Johns Hopkins), Instructor in Chemistry, State Normal School, Lowell, Mass. Boston: D. C. Heath & Co. 1903. pp. 590.

The title of this text-book accurately describes its contents. The treatment of the subject is essentially descriptive, and the author states that the volume is prepared "for teachers who wish to emphasize the facts, laws, theories, and applications of chemistry."

The text-book is divided into two parts, the first of which contains the descriptive text, together with the exercises and problems, and the second contains the experiments. The

text is divided into 31 chapters, the order in which the topics are presented being essentially that which is usually adopted. The discussion of law and theory follows the chapters treating successively of physical and chemical change, oxygen, hydrogen, water, and nitrogen and the atmosphere, while Gay-Lussac's law, Avogadro's hypothesis, and vapor-density follow the chapters on chlorine and hydrochloric acid, ammonia, and the oxygen compounds of nitrogen. The chapter treating of phosphorus, arsenic, antimony, and bismuth connects the non-metals with the metals, and the closing chapters of the text treat of the periodic law and spectrum analysis, and a description of representative members of the important classes of organic compounds. Each chapter is followed by a series of questions which serve at once as a means of review for the student and a valuable incentive—under encouragement from the teacher—to further reading. Stoichiometrical problems also accompany each chapter. An appendix contains data concerning the metric system, thermometry, crystallography, brief notes of chemical history and biography, atomic weights, and a list of reference books and supplementary reading. An admirable feature of the book is the introduction of the protraits of eminent chemists, which are distributed through the text.

The experiments of Part II. "have been prepared to meet the needs of those schools in which the laboratory facilities are limited or the time for chemistry is short." The experiments appear to be carefully and happily selected although one can hardly escape the notion that the omission of the carefully prepared quantitative experiments which characterize his "Experimental Chemistry" has cost the author at least a sigh of protest and regret. From the present volume and the "Experimental Chemistry" taken together, it is surely possible to make a selection of quantitative or qualitative experiments which will be in accord with the most varied opinions. For those who prefer the experiments of the earlier volume as they stand, Part I. of this text-book is bound separately.

In these days of overcrowded curricula, overcrowded school rooms, and overtaxed energies, it is increasingly essential that the chemical instruction in our schools should be of such a character that it will broaden the pupil's horizon, hold his interest, and be within his grasp, and also of such a character that the instructor may hope to attain positive results with a minimum of attention to the individual, in many cases. Such a course can readily be selected from the experiments so care-

fully laid down in Dr. Newell's two books, and, whatever the nature of the course chosen may be, the text of the present volume must become an efficient aid. The statements are simple, direct, and clear, although the statement regarding chemistry (page 1), possibly because of its prominence, seems to suggest the criticism that it is less fortunately expressed than most others, and less so than the corresponding statement (page 15) of the author's earlier work. Unusual pains have been taken to eliminate errors of statement and to secure accuracy in proof-reading.

In the general treatment of the subject there is not much that is unique in this text-book; the features which chiefly characterize it are its carefully considered statements, and the suggestive aids to study to be found in the questions, problems, and material in the appendix, all of which are plainly the outcome of earnest and thoughtful teaching. The book cannot fail to be of value to its readers—both teachers and pupils—whatever small differences of opinion there may be regarding the choice of some particular experiment, or form of phraseology.

It may fairly be regarded as a noteworthy addition to the host of text-books for school use, and if the teachers who make use of the manual will catch the spirit in which the volume has been written it will help to promote the adoption of rational courses in chemistry in secondary schools, which will be serviceable alike for those who expect to pursue the subject later in college, and for those whose chemical horizon must be bounded by the confines of their school instruction.

H. P. T.